Methods for Preparation of Catalytic Materials

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I. Introduction

Catalytic materials exist in various forms and their preparation involves different protocols with a multitude of possible preparation schemes, many times larger than the number of known catalysts. Moreover, preparation of any catalyst involves a sequence of several complex processes, many of them not completely understood. As a result, subtle changes in the preparative details may result in dramatic alteration in the properties of the final catalyst. Our objective in this review is to provide the various preparative procedures available to create catalytic materials. To accomplish this objective, we sought the most recent literature. Our review, therefore, focuses on research reported mainly in the past five years.

The goal of a catalyst manufacturer is to produce and reproduce a commercial product which can be used as a stable, active, and selective catalyst. To achieve this goal, the best preparative solution is sought which results in sufficiently high surface area, good porosity, and suitable mechanical strength. The first of these, surface area, is an essential requirement in that reactants should be accessible to a maximum number of active sites. The properties of a good catalyst for industrial use may be divided, at least for the purpose of easy classification, into two categories: (1) properties which determine directly catalytic activity and selectivity, here such factors as bulk and surface chemical composition, local microstructure, and phase composition are important; and (2) properties which ensure their successful implementation in the catalytic process, here thermal and mechanical stability, porosity, shape, and dimension of catalyst particles enter. The requirements which are fundamental for catalyst performance generally require a compromise in order to produce a material which meets the contradictory demands imposed by industrial processes. An acceptable solution is typically ascertained by a trial-and-error route. Catalytic materials become catalysts when they are used in industrial processes.[1] A way this can be realized occurs when the variety of methods used to prepare catalytic materials are viewed in relation to their successful implementation in commercial applications.

In our attempt to develop the elements for a scientific basis for catalyst preparation, we return to the fundamental "blending" and "mounting" procedures used to prepare catalytic materials. Figure 1 is a simplified diagram which summarizes the traditional methods used for the preparation of heterogeneous catalysts. The vertical ordering takes into account the fact that the final catalyst is a solid phase with new properties which have to be acquired and stabilized during the preparation process while the horizontal delineation depicts the various methods for "blending" and "mounting" to produce the catalytic material. A noticeable discontinuity does develop here, however, because some preparative procedures can fit into both cases.

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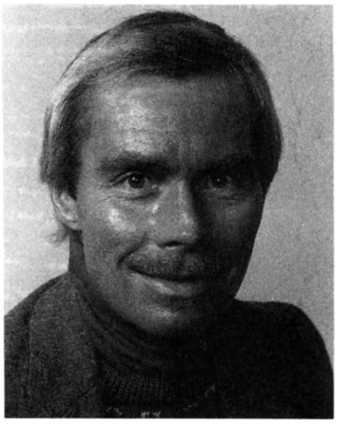
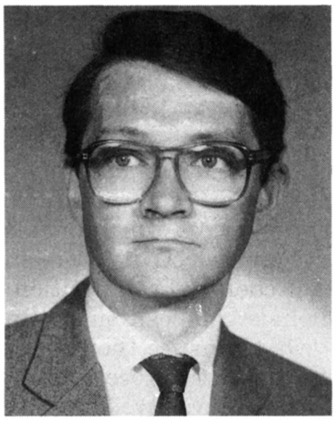


Jim Schwarz was born in the early 1940s, experienced the "Sputnik" era of the 1950s, and finally grew up in California in the 1960s where he received his Ph.D. from Stanford University. After a series of post doctoral positions at Cambridge University, U.C. Berkeley, and (back again) Stanford, he established his industrial credentials at Chevron Research and then Exxon. In 1979, he was appointed Associate Professor of Chemical Engineering and Materials Science at Syracuse University. In a timely fashion, his title was changed to Professor; his scientific interests focus on phenomena occurring at interfaces. He fills his daily life with a balance between pursuits of the mind and the body.



Cristian Contescu was born in Galati and raised in Tulcea, Romania, two cities on the border of the Danube. After he received a B.A. in Physical Chemistry from the University of Bucharest (1971), he joined the Institute of Physical Chemistry in Bucharest and received a Ph.D. from the Polytechnical Institute in Bucharest (1979). His interest has always focused on the study of interfaces but has shifted from phenomena at the gas–solid interface studied by field emission microscopy to the problems of catalyst preparation and phenomena at the solid–liquid interface. In 1992, he joined Professor Schwarz's group at Syracuse University as a visiting research associate. He enjoys classical music, literature, and fine arts.

Adriana Contescu was born in Argetoaia, Romania, and raised in Oltenia, a rich county in southern Romania. She received her B.A. in Inorganic Chemistry from Bucharest University (1971) and a Ph.D. from the Polytechnical Institute in Bucharest (1984). After joining the Institute of Physical Chemistry in Bucharest in 1979, her research concentrated on the chemistry of polynuclear inorganic complexes and nonconventional routes for the preparation of mixed oxides. This review paper is a result of her 1993 visit to Syracuse University. Her spare time pursuits include needlework, gardening, and playing with her dog.

In Figure 1, two preparation routes define the extremes of traditional procedures used in catalyst preparation: precipitation (with the variant of coprecipitation) and impregnation (with such variants as ion exchange, deposition, and grafting). In the precipitation route, a new solid phase is obtained by the "blending" of proper reagents (precipitating agents) from a liquid medium; the resulting precipitate is transformed in subsequent preparation stages into the active catalyst. During these transformations, both the mechanical properties of the catalyst and those intrinsically related to the catalysts' performance have to be considered simultaneously. In contrast, in the impregnation route, a solid phase preformed in a separate process is used as a support, and the catalytically active material is "mounted" and stabilized on it. In this way, at least a part of the mechanical properties of the final catalyst are controlled by the preexisting support, and the preparation process is basically focused on the introduction of the catalytic compound(s). Between these two extremes there lies methods which are best characterized as solid transformation. Here physical and chemical processes are used to reconstruct a solid into a form that meets the demands imposed by the processes in which they will be used.

To establish guidelines for the development of a scientific basis for catalyst preparation is perhaps a very ambitious goal. We would be required first to answer the following rhetorical questions:

- What are the properties which determine the performance of a catalytic material?
- How can these properties be introduced, developed, and/or improved during preparation?

The answer to these questions involves a comprehensive discussion of the theories of catalysis, which is beyond the scope of our review. We will attempt, instead, to provide a rationale for each reader to answer these questions on the basis of his/her own interests. We start our discussion by describing the fundamental steps in producing bulk catalysts and/or catalyst supports. The fundamental processes involved are those derived from traditional three-dimensional chemistry. The topic areas will include single-component and multicomponent metal oxides. Unsupported metallic catalysts are formed by transformations involving physical or chemical processes, and the preparation methods for this class of materials will be discussed next. Our attention will then turn to the preparation of supported catalytic materials. The main topics to be discussed will be those related to the interaction between the support and the active phase when they are put together to generate the catalyst. In this approach, we exploit the virtually unexplored field of surface, or two-dimensional, physical chemistry. The materials considered include dispersed metals and alloys and composite oxides.

We recognize that this organization might seem arbitrary and that the reader might equally propose

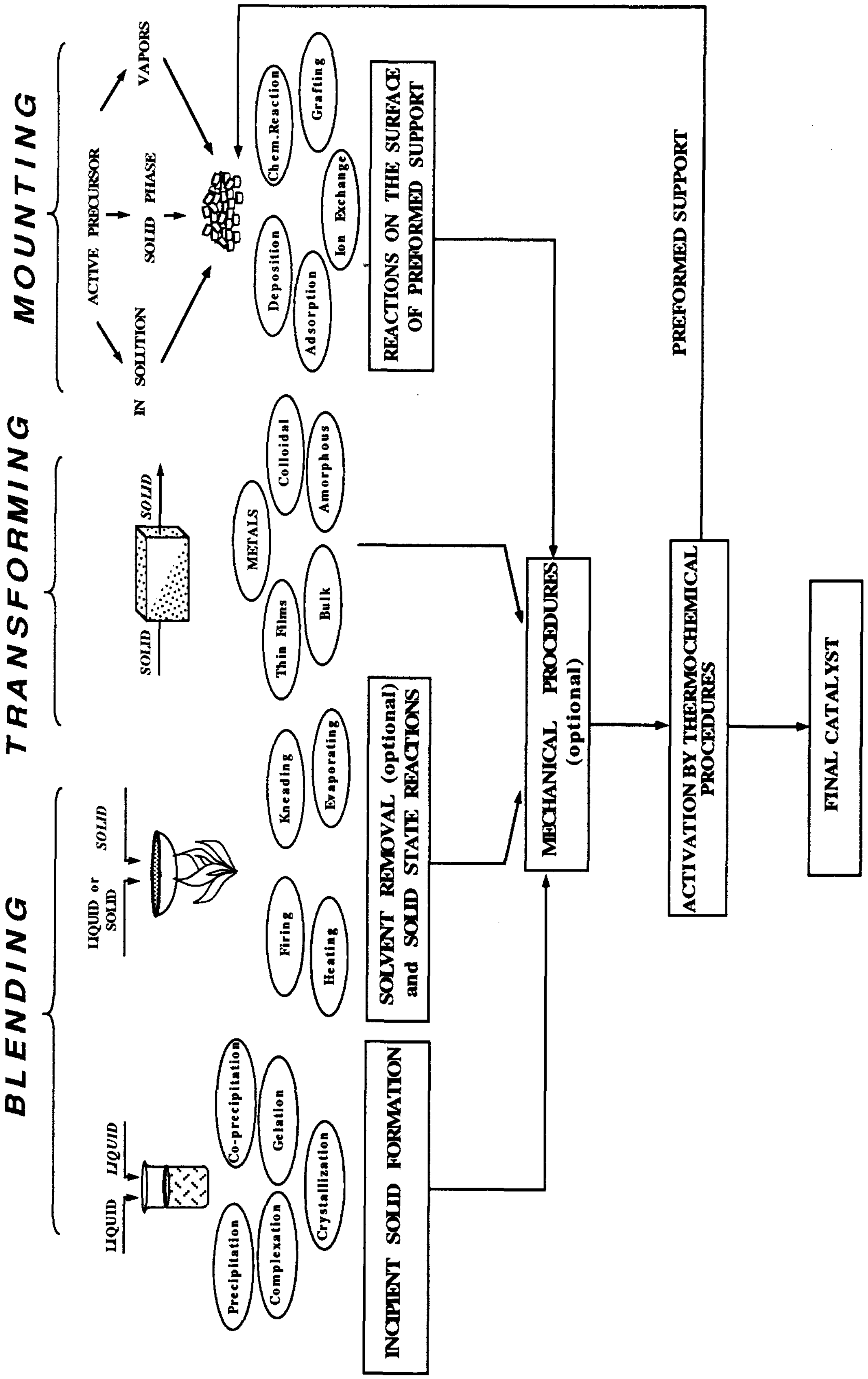


Figure 1. Simplified diagram summarizing methods of blending, transforming, and mounting catalytic components.

a different classification scheme. The difference between supported and unsupported (or bulk) catalysts is not always apparent. Even bulk catalysts or supports, usually thought to have uniform chemical composition, may present a multiphase structure that might be the result of either doping, promoting, surface or bulk segregation, or even the effect of the reaction environment on the catalyst. We prefer the above organization in that, from one point of view, there are only two main routes for the preparation of almost all catalysts. These can be divided into the two categories: methods in which the catalytically active phase is generated as a new solid phase by either precipitation or a decomposition reaction, and methods in which the active phase is introduced and fixed onto a preexisting solid by a process which is intrinsically dependent on the surface of the support.

II. Three-Dimensional Chemistry

Recent years have witnessed marked progress in the preparation of stable catalytic materials, many of them with potential applications as catalysts. This success has been achieved by either the selection of a suitable support or by choosing a proper method of preparation, or by a combination of both approaches.

The simplest kinds of catalysts, from a structural point of view, are single phase catalysts, such as bulk metals and alloys, bulk oxides, sulfides, carbides, borides, and nitrides. These materials are, more or less, uniform solids at the molecular level that exhibit catalytic properties on their external surface. Therefore, these materials are preferably used in a physical form which allows for a maximum development of contact of the surface of the material with its environment. To this end, preparation methods are selected which avoid excessive heat treatments which would result in the system acquiring a more stable lower surface energy state at the expense of its active surface.

Bulk oxide catalysts, either single metal or multimetal, used in industrial processes are usually in the form of powders, pellets, or tablets, with either amorphous or polycrystalline structure. The most common method used for preparation of bulk oxide catalysts is the (co)precipitation of a precursor phase, followed by thermal transformation that leads to the oxidic phase. The ceramic method involving grinding and firing mixtures of oxides is not very convenient for preparation of oxide catalyst because of the high temperatures needed. Thus, the trend in the development of preparation methods has witnessed efforts to eliminate the high-temperature treatments of the coprecipitated materials (such as calcination of mixtures of hydroxides and decomposition to oxides) which affect the solid state reactions that produce the intimately mixed oxide phase that acts as a catalyst. Several alternative preparation routes that enable a better mixing of the components have been proposed. A method of continuous homogeneous precipitation was developed, wherein the precipitating agent (hydroxyl ions in the classical coprecipitation method) is slowly and continuously generated in the synthesis medium by a controlled hydrolysis process (such as hydrolysis of urea). The advantage of slow precipitation is a more efficient mixing of the components in the precipitated product. The sol–gel method, although related to the coprecipitation method, provides better control of the texture of the resulting catalyst and ensures an increased uniformity of the product. The method consists in formation of a colloidal dispersion of the metal constituents, usually by hydrolysis of metal alkoxides. The colloidal solution is then subjected to gelation by either changing the pH, the temperature, or the electrolyte. The resulting gel is then heat treated to remove the solvent. Decomposition of coordination compounds, including polynuclear compounds, is another preparative route that starts from a precursor where the metallic elements are intimately mixed at the molecular or at the atomic level. Among the metal complexes that can be decomposed at relatively low temperatures are oxalates, formates, citrates, and carbonyls.

Bulk sulfide catalysts and mixed sulfide catalysts are prepared most commonly by either direct sulfidation (i.e., reaction with hydrogen sulfide) of oxides, halides, or other metal salts. The direct method may require the use of high temperatures. A second variant is the decomposition of a sulfur-containing precursor, such as a thiosalt, which is obtained by low-temperature precipitation. A type of low-temperature coprecipitation is homogeneous sulfide precipitation, wherein the mixing of the metal salts is made before any addition of the precipitant.

Recently, a new genre of single phase catalysts has emerged in which the entire solid rather than just the external surface is involved in catalysis. The new materials are crystalline solids which contain active sites uniformly distributed throughout their bulk at the intracrystalline level. This family of uniform heterogeneous catalysts, generally referred to as molecular sieves, includes microporous zeolites, aluminum phosphates, with metal- and silicon-substituted analogs, layered compounds such as clays and their pillared variants, layered oxides with perovskite structures, and heteropolyacids with a liquid-like behavior. The possibilities for preparation of materials in this class are vast since they exploit the virtually unlimited number of ways to link together atomic units in a crystalline or polymeric structure. Their methods of preparation consist of a combination of chemical (precipitation, leaching) and physical (supercritical crystallization) procedures.

The common features of all the preparation methods summarized above for bulk catalytic materials is the use of traditional methods and techniques from preparative chemistry, such as precipitation, hydrolysis, and thermal decomposition. The chemistry involved during these preparation steps does not differ much from that taught in classical handbooks of analytical or inorganic chemistry. These processes involve mixing of solutions, blending of solids, precipitation, filtration, drying, calcination, granulation, tableting, and extrusion. In other words, the chemistry involved is three dimensional with the meaning that it is isotropic with respect to the container in which it is done.

A. Liquid–Liquid Blending

The method of precipitation is the best known and most widely used procedure for synthesis of both monometallic and multimetallic oxides. Precipitation results in a new solid phase (precipitate) that is formed discontinuously (i.e., with phase separation) from a homogeneous liquid solution. A variety of procedures, such as addition of bases or acids, addition of complex-forming agents, and changes of temperature and solvents, might be used to form a precipitate.

The term coprecipitation is usually reserved for preparation of multicomponent precipitates, which often are the precursors of binary or multimetallic oxidic catalysts. The same term is sometimes improperly used for precipitation processes which are conducted in the presence of suspended solids.

Depending on the particular application, the newly formed solid phase may be further subjected to various treatments, such as aging and hydrothermal transformation, washing, filtration, drying, grinding, tableting, impregnation, mixing, and calcination. During all these preparative steps, physicochemical transformations occur which can profoundly affect the structure and composition of the catalyst surface and even its bulk composition. If the adage the catalyst "remembers" how it was prepared, even after being subjected to various heat treatments at elevated temperatures is valid, then any cause-and-effect correlations that can eventually be made between the precipitation procedures and the final characteristics of the catalyst becomes significant.

1. Precipitation

A scientific approach to the preparation of catalysts by precipitation routes was introduced by Marcilly.[2,3] The formation of the precipitate from a homogeneous liquid phase may occur as a result of physical transformations (change of temperature or of solvent, solvent evaporation) but most often is determined by chemical processes (addition of bases or acids, use of complex forming agents). In almost all cases, the formation of a new solid phase in a liquid medium results from two elementary processes which occur simultaneously or sequentially: (1) nucleation, i.e., formation of the smallest elementary particles of the new phase which are stable under the precipitation conditions; and (2) growth or agglomeration of the particles.

Marcilly[2,3] stressed the importance of supersaturation, among other factors such as pH, temperature, nature of reagents, presence of impurities, and method of precipitation in determining the morphology, the texture and the structure of the precipitates. For example, under conditions of high supersaturation, the rate of nucleation of solid particles is much higher than the rate of crystal growth and leads to the formation of numerous but very small particles. Under the condition when the critical nucleation size is very small, only a metastable and poorly organized phase can develop; this may further change to a more stable phase during the hydrothermal treatment of the precipitates.

Obtaining high supersaturation conditions is a difficult task in practice because of the natural evolution of the system toward a decrease of supersaturation by nucleation of solid particles and consumption of reagents. High levels of supersaturation can only be obtained for a short time and within limited volumes of solution. The problem of obtaining a homogeneous precipitate with respect to the size and structure of the particles reduces to that of achieving a uniformly high level of supersaturation throughout the liquid before the nucleation starts, which may be quite difficult because of mass and heat transport limitations.[2]

The chemical and physical properties of the precipitates kept in contact with their mother liquor may change, often substantially, due to secondary processes taking place in the suspension. One of these processes, known as Ostwald ripening, leads to an increase in the particle size of a precipitate. Because the solubility increases with decreasing particle size, small particles begin to dissolve and large crystals continue to grow. Another process which takes place during aging of precipitates is agglomeration of colliding particles as a result of either Brownian motion or imposed mechanical forces.

The most common catalysts derived from precipitation are aluminas. In order to emphasize the significance of the variables described above on the physicochemical properties of the finished material, we will devote some effort to outline the procedures used to formulate aluminas. Because of its industrial importance, the preparation of aluminas of controlled porosity and surface area continues to be the focus of a large number of investigations.[4-7]

Studies on the preparation of alumina in the absence of additives showed that the pore size distribution and the surface area are determined mainly by conditions of precipitation and aging. Development of these properties is due to the interconversion of amorphous hydroxide, pseudoboehmite, and bayerite formed during precipitation.[4]

Washing and drying were found to have little influence on texture for samples precipitated from ammonia and aluminum nitrate but contributed to the enlargement of pores when NaOH was used in precipitation. More control is possible by the use of additives.[8] Alcohols added before precipitation of aluminum hydroxides only had an effect on the pore size when their adsorption on the precipitate was strong enough to replace the "solvent barrier" at the surface of precipitates. With these additives, the solubility of precipitates is decreased, leading to decreased Ostwald ripening and thus encouraging aggregation by particle bridging. Alcohol washing after precipitation produces higher surface areas and higher mesoporosity due to lower surface tension and less pore collapse during calcination.[5]

The thermal and physical characterization of the conversion of pseudoboehmite to γ-Al_2O_3 were reviewed,[9] and the relationship with the manufacturing route of the pseudoboehmite powder was shown. In general, physical properties like particle size and shape, crystallinity, and porosity have a distinct influence on the thermal behavior of pseudoboehmite powders. Better characterization of thermal and physical properties has allowed one to improve catalyst manufacturing at the industrial level. Unit operations such as mix-mulling, extrusion, drying, and calcination are clearly affected by powder characteristics.[10]

The calcination step may induce further changes in the texture of the finished supports. Under conventional operation conditions, γ-Al_2O_3 is stable, but at temperatures between 1250 and 1350 K a phase transformation through metastable δ- and θ-Al_2O_3 leads to formation of α-Al_2O_3. The process is accelerated by steam[11] and results in a drastic drop in surface area which is caused by sintering of primary particles. The versatility of alumina to be produced with a broad range of surface areas and pore size distributions is in part due to the phase transformations during calcination.

A systematic study[6,7] of aluminum oxides obtained by heat treating of γ-Al_2O_3 showed that a monodisperse structure is preserved below 1375 K, with a slight increase in the average pore radius. Formation of the α-Al_2O_3 phase is related to the generation of a new system of wider pores that again becomes monodispersed when the α-phase is completely formed.[6] A relationship between porosity and mechanical strength was proposed for alumina catalyst supports.[12,13]

A number of studies report methods to increase the thermal stability of γ-Al_2O_3 particles by introducing various additives. The subject was recently reviewed in relation to preparation of stable materials for high-temperature combustion.[14] For example, it was reported[15,16] that several ions (In^{3+}, Ga^{3+}, and Mg^{2+}) have an accelerating influence while others (Zr^{4+}, Ca^{2+}, Th^{4+}, La^{3+}) have an inhibiting action during the transformation of aluminas to the α-phase. The effect of thermal stabilizing modifiers is due to surface nucleation of stable compounds, which by interaction with the underlying alumina,[17,18] results in the formation of an aluminate surface layer which prevents transformation of γ to α alumina[19] but may also modify the Lewis acidity of alumina.[20] According to other results,[21,22] addition of alkaline earth metals (Ca, Sr, Ba) increased the ability to preserve a high surface area (≥ 5 m^2 g^{-1}) after calcination at 1700 K. Since small $BaO{\cdot}6Al_2O_3$ crystallites prepared through a coprecipitation route had a similar sintering resistance, it was concluded that formation of barium hexaaluminate is a promising option for stabilizing combustion catalyst supports.[14]

An alternate method to achieve the thermal stabilization of alumina without foreign additives was also reported.[23] Since the transition of metastable phases to α-Al_2O_3 occurs predominantly at the contact between primary particles, the key for suppressing the rate of sintering without additives is preparing active aluminas in a morphological state in which the area of contact between primary particles is minimized. Alumina prepared by fume pyrolysis of sols consists of fibrillar boehmite, approximately 100 nm in length and 10 nm in diameter. After calcination at 1473 K for 30 h, the material maintained a surface area of 50 m^2 g^{-1} and still consisted of fibrils. This was ascribed to the suppression of the phase transformation to α-Al_2O_3.

New classes of catalyst supports, which are used in demanding reactions, are beginning to receive attention. For example, the conditions for preparation of magnesium oxide, which is the catalyst used for oxidative coupling of methane to ethane and ethylene, has gained the recent attention of several researchers.[24-26] In the case of $Mg(OH)_2$ as the starting reagent, washing with alcohol of the hydroxide precipitate leads to a drastic decrease in surface area of the calcined MgO. The effect was ascribed to formation of surface alkoxides and induction of particle–particle bridges through surface condensation reactions.[25] This process favors the development of order in the precipitate. The bridges formed during washing were maintained through the calcination step. Also, the morphology of $Mg(OH)_2$ precipitates was found to be dependent on whether the pH during precipitation and aging was above or below the isoelectric point (pH = 12). This demonstrates the influence of the electric charge of primary particles on their tendency toward aggregation.

2. Coprecipitation

In the synthesis of multicomponent systems, the problems are even more complex. Coprecipitation rarely allows one to obtain good macroscopic homogeneity. In a system with two or more metallic compounds, the composition of the precipitate depends on the differences in solubility between the components and the chemistry occurring during precipitation. Generally, under the conditions of either a slow precipitation rate or poor mixing within the reaction medium, coprecipitation is selective and the coprecipitate is heterogeneous in composition. Subsequent to formation of the coprecipitate, hydrothermal treatments which transform amorphous precipitates to crystalline materials with improved thermal stability and surface acidity may be carried out.[27] This procedure is widely applied to prepare molecular sieves.

Depending on the composition of the precipitate formed, two chemical routes should be distinguished in the coprecipitation procedures. The simplest case is that of sequential precipitation of separate chemical compounds. This occurs whenever there is a large difference in the solubility products of the compounds involved. The so-called "coprecipitates" of hydroxides, hydroxo carbonates, oxalates, and formates containing two or more different metals are generally nonhomogeneous in composition and only very seldom generate a homogeneous mixed oxide[28] by solid phase reactions at high calcination temperature. Doping or substitution of ions in these precipitates is difficult because of the different reactivities involved.

The second possibility is the formation by coprecipitation of a well-defined chemical compound which might serve as a chemical precursor from which the final catalyst is obtained.[29-31] The intermediate compound must be easily decomposed under mild calcination. This route is preferred whenever a better intimate mixing of the catalyst components is desired. The metal ratio in the precursor compound is, however, restricted to a quite rigid stoichiometry.

Crystalline stoichiometric precipitates formed by several metal oxyanions (vanadates, chromates, tungstates, and molybdates) and a second metal cation may be further used to obtain an intimate interdispersion of the two metals. As an example, the activity of Cu/Cr catalysts depends on the amount of copper chromate, $CuCrO_4$, formed during their preparation, and this is the precursor of the most active sites of the final catalyst.[32] In another example, precipitation from nitrate solutions of Fe, Co, and Bi with ammonium heptamolybdate gave molybdenum heteropolycompounds containing Keggin-type anions, $[MMo_6O_{24}H_6]$, where M = Bi or Fe, which are the precursors of the corresponding molybdates by solid phase reactions.[33]

Other intermediates extensively studied as catalyst precursors comprise the class of mixed-metal hydrated hydroxo carbonates with a layered structure. Thus, during preparation of active copper catalysts used for synthesis of hydrocarbons or methanol by hydrogenation of CO,[34] the copper phase must be obtained highly interdispersed with at least one other oxide component. This structure stabilizes the very small Cu^0 particles and favors further interaction of copper with the host oxide.[35] A high degree of homogeneity at the atomic level for this class of catalysts may be achieved by decomposition of single phase precursors, such as either the hydroxo carbonates with the aurichalcite structure, $(Cu,Zn)_5(CO_2)_2(OH)_6$, from which binary Cu/Zn catalysts are prepared or with the lamellar hydrotalcite-type crystalline structure, $(Cu,Zn)_6(Al,Cr,Ga,Sc)_2(CO_3)(OH)_{16}$, used for preparation of highly active ternary catalysts, Cu/Zn/(Al,Cr,Ga,Sc). The details of precipitation of these single phase precursors involve a careful control of pH and the rate of precipitation;[36] the morphology of the precursor may influence the degree of interdispersion of the final multiphase catalyst.[37] In these systems, because all elements are homogeneously distributed in the hydrotalcite phase, no surface segregation is observed and pseudomorphic thermal decomposition[38] leads to a spinel-type oxide. The limits between which the ratio of metals in the catalyst may be varied depends on the stoichiometry and structure of the single phase precursor: for the Cu/Zn binary aurichalcite, it may be changed between quite large limits (0.02 to 0.30), while the structure of the ternary hydrotalcite allows the Cu/Zn/Me^{III} ratio to be varied within much narrower limits; a typical value for single phase precursors of copper-based catalysts is 30/45/25.[39] The hydrotalcite-like coprecipitated precursors were recently used as intermediates for the preparation of other nonstoichiometric spinel-type catalysts, with the general formula $M_{1+y}Cr_{2-2y}/3O_4$ (M = Zn, Cu, Co); they are employed as catalysts for specific hydrogenation reactions.[38,40]

With a proper selection of metals and complexing agents, precipitation of mixed-metal polynuclear coordination compounds is possible. The use of coordination compounds as raw materials is a nonconventional procedure to prepare mixed oxides by a mild thermal decomposition.[41-43] Recent literature in inorganic chemistry often makes reference to synthesis and characterization of several types of binuclear coordination compounds with molecularly organized structures that contain metals of interest for preparation of catalysts. For example, mixed-metal complexes in the general series $\{NBu_4[MCr(ox)_3]\}_x$ (where NBu^{4+} = tetrabutylammonium ion, ox^{2-} = oxalate ion, and M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) form a three-dimensional structure comprised of alternate arrays of Cr(III) and M(II) metals.[44] Also, in the series of μ-oxo-trinuclear mixed-metal carboxylate complexes,[45] $[M_2^{III}M^{II}O(ac)_6L_3]\cdot nL$, where M^{III} = Fe, Co, Cr, M^{II} = Fe, Co, Ni, Zn, Mn, Mg, and L = py, H_2O, the molecular structure is composed of trinuclear, oxo-centered $M_2^{III}M^{II}O$ units. It is known that thermal decomposition of polynuclear coordination compounds of the latter type yields mixed oxides with spinel structures.[46] This suggests the use of other coordination compounds such as those mentioned above as potential precursors for the binary mixed oxides in the system $CuO-ZnO-Cr_2O_3$. For the moment, preparation of ternary mixed-metal compounds remains a more difficult task.

Polynuclear mixed metal complexes deserve more attention as precursors for the preparation of catalysts. This methodology has the advantage that the component metal ions are intimately bound in the molecular structure of the polynuclear compound and a homogeneous mixed-oxide phase or a composite oxide is more easily formed after either a mild decomposition or a hydrothermal treatment at moderate temperatures.

Finally, a new approach to the precipitation method is the use of organic solvents as precipitation media. The colloid chemistry is not easily extrapolated from the aqueous phase to organic systems. In addition, organic solvents pose practical problems to catalyst manufacturing, but these difficulties can be offset by the special properties of catalysts precipitated from organic solvents.[1] As an example, two procedures can be summarized for the preparation of VPO catalysts for selective oxidation of butane to maleic anhydride:[47] (a) reduction of V_2O_5 or NH_4VO_3 in aqueous medium, followed by addition of H_3PO_4 or (b) reduction of V_2O_5 in an organic medium, using isobutyl or isopropyl alcohol, followed by addition of H_3PO_4. The catalysts prepared in organic media are more active. A possible explanation is that the precursor obtained by precipitating V_2O_5 and H_3PO_4 in an organic medium has a macrostructure consisting of sponge-like spherical particles which are not obtained by precipitation in aqueous media.[48] Since the catalyst is activated through a topotactic transformation:

$$2VOHPO_4\cdot(H_2O)_{0.5} \leftrightarrow (VO)_2P_2O_7 + 2H_2O \quad (1)$$

it is conceivable that the catalyst obtained in organic media has more accessible active sites than the catalyst obtained from the aqueous route. The difference in the texture corresponds to a high-performance catalyst which has found commercial recognition. In this example, the precursor acts as an improved matrix for the crystalline growth of the oxide active phase during the topotactic transformation.[49] The properties that the solid will develop as a final catalyst are strongly affected by all structural and morphological changes which occur during the topotactic transformation.[50-52]

3. Complexation

The composition of the homogeneous phase can be used to exploit the high binding affinity of metal ions which will result in catalytic materials with properties that differ from those derived from (co)precipitation procedures. The complexation method makes use of chemical reactions which transform slowly and without physical discontinuity (i.e., without phase separation) the homogeneous solution of catalyst precursors into a homogeneous, amorphous phase, with either a glassy, jelly-like, or foamy appearance. This precursor is then dried and decomposed to yield better intermixed and more highly dispersed oxides than those prepared by the usual precipitation routes. The procedure has also been called the method of an amorphous intermediate.[53]

To obtain a smooth gelation of the homogeneous solution of catalyst precursors, they are complexed or chelated with multifunctional organic reagents that are capable of entering in a successive series of intermolecular polycondensation reactions. The gelation process results in a three-dimensional organic network with the metallic components entrapped in this structure. The organic matrix is responsible for the textural properties such as pore structure or surface area of the catalyst.

The search for the appropriate catalyst precursors, solvents, and complexing agents lead to the development of variants of the chemical mixing method. According to the original proposal by Courty and Marcilly,[3,53] the metallic elements are added as water-soluble salts, and various α-hydroxy acids are used as complexing agents. Because citric acid was more frequently used (several other acids, such as malic, tartaric, glycolic, and lactic can also be equally employed), the complexing method has also been called the "citrate method". This method was recently used to prepare oxide solid solution $La_{0.9}Sr_{0.1}O_{1.45}$ catalysts for the methane coupling reaction.[54] In the ternary Cu/Co/Al system, catalysts were prepared with atomic ratios (Cu + Co)/Al and Cu/Co covering a much broader range than that allowed by the rigid stoichiometry of the hydrotalcite precursors that could be formed by coprecipitation.[55]

A more general procedure, named by the authors the "chemical mixing" method, was proposed by Mizukami and Niwa.[56,57] They introduced metallic components as either soluble salts (nitrates, chlorides, acetates) or metal–organic compounds (alkoxides or β-diketone complexes) and used polar solvents with at least two complex-forming functionalities (diols, keto alcohols, and amino alcohols) to obtain homogeneous solutions. In the gelation step, coagulation occurs by hydrolysis and intermolecular condensation reactions and a three-dimensional polymeric network is finally produced. At this stage, the components are uniformly incorporated within each other and the homogeneity of the initial solution is maintained (as schematically shown in Figure 2). The mixed oxides obtained by decomposition were much more effective catalysts than their counterparts prepared by conventional precipitation or kneading.

A related procedure was used by Busca and Lorenzelli[58–60] to prepare amorphous alumina with zeolite-type microporosity. They reacted aluminum nitrate with organic agents (glycerol, tartaric acid) and decomposed the spongy bulky solid that resulted. Addition of other glass-forming elements, such as phosphorous or boron, inhibited both the crystallization and the γ- to α-alumina phase transition. High surface area, amorphous aluminas, with controlled pore size (10–15 Å) and surface acidity, can be prepared by this method.

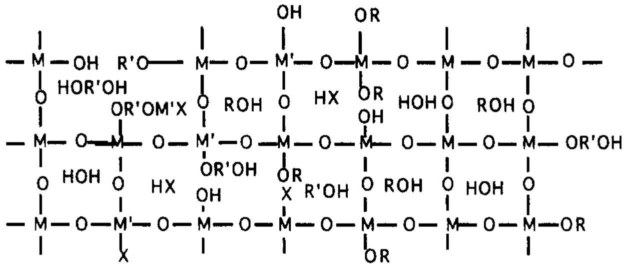


Figure 2. Mixed-metal gel depicting homogeneity of structure.

A common characteristic of all the above variants of the "complexing" or "chemical mixing" methods is the use of organic molecules with multiple chemical functionalities as templates for formation of the three-dimensional network during the gelation step. Removal of the organic ingredient is a critical step during catalyst activation. A highly exothermic, uncontrolled decomposition was reported for glassy precursors containing metals active for oxidation reactions.[61] This could be avoided if decomposition was carried out under an inert atmosphere.[55] Incomplete burning of the organic ingredient during thermal decomposition of the amorphous precursor usually results in uncontrolled carbon contamination of the catalyst.[53] These inconveniences can be eliminated by using sol–gel methods, in which the gelation step is better controlled.

4. Gelation

In contrast with the (co)precipitation route, which is a discontinuous transformation, the gelation route (also known as the sol–gel method) is a homogeneous process which results in a continuous transformation of a solution into a hydrated solid precursor (hydrogel). Sol–gel methods have been recognized for their versatility which allows control of the texture, composition, homogeneity, and structural properties of the finished solids. The applications of the sol–gel method to catalyst preparation were reviewed recently[62] with special emphasis on the broad range of possibilities offered by this method to prepare tailored materials, such as dispersed metals, oxidic catalysts, and chemically modified supports.

The nanoscale chemistry[63] involved in sol–gel methods is a more straightforward way to prepare highly divided materials. Within the general context of sol–gel methods, it is possible to find examples of all major types of catalysts. Hydrosols are formed during precipitation of hydrous oxides. The network that results by aggregation of primary sol particles may either extend quasiinfinitely throughout the volume of the specimen (gel) or may be discontinuous (flocculates). Gels dried by simple evaporation of the liquid which interpenetrates their framework always suffer from pore shrinkage with a concomitant irreversible reduction of their surface area (xerogels). The collapse of the pore structure is caused by mechanical forces due to retreating water menisci in the pores. It can be avoided by either replacing water with another liquid with lower surface tension before drying or by removing water vapor at a temperature higher than its critical point (aerogels). The major breakthrough in the sol−gel methods for catalyst synthesis came with the discovery of new and faster methods to produce aerogels which subsequently lead to their application in large-scale synthesis.

The method proposed in 1968 by Nicolaon and Teichner[64] for preparation of silica aerogels was immediately extended to the synthesis of many other systems of mono- or multicomponent oxides. The method is based on the hydrolysis and gelling (for instance by controlled addition of water) of alkoxides or other reactive compounds in alcoholic solutions.[65−67] The chemistry of the processes which occur during the sol−gel synthesis can be represented by the following sequence of acid- or base-catalyzed nucleophilic additions or substitutions:[68]

hydrolysis (hydroxylation) of the metal alkoxides

$$\text{M-OR} + H_2O \leftrightarrow \text{M-OH} + \text{R-OH} \quad (\text{M} = \text{metal or Si; R} = \text{alkyl}) \quad (2)$$

olation (condensation with formation of hydroxy bridges)

$$\text{M-OH} + \text{M-OHX} \leftrightarrow \text{M-OH-M} + \text{X-OH} \quad (\text{X} = \text{H or R}) \quad (3)$$

oxolation (condensation with formation of oxygen bridges)

$$\text{M-OH} + \text{M-OX} \leftrightarrow \text{M-O-M} + \text{X-OH} \quad (\text{X} = \text{H or R}) \quad (4)$$

The overall process produces a highly reticulate, metastable polymer with an open structure in which the primary units are held together by either chemical bonds, hydrogen bonds, dipole forces, or van der Waals interactions. This framework is imbibed by the solvent. In order to transfer this structure into the solid phase, the liquid within the gel must be removed in such a way that a liquid/vapor interface is not formed. Aerogels are obtained when the gel is dried by supercritical extraction. This procedure is conducted by high-pressure heating, which transforms the liquid contained in the gel into supercritical vapors, and eventually is followed by gradually diminishing the pressure at a constant supercritical temperature. Under supercritical conditions, the structure of the gel is conserved in the solid state without collapsing. Another way to avoid a liquid/vapor interface requires that the liquid first be frozen and then sublimed. The resultant aerogel is called a cryogel, since cryogenic conditions are normally involved in drying.

The three-dimensional network in the aerogel structure consists of tetrahedrally coordinated units, MO_4, in a loosely packed configuration. One of the most striking properties of aerogels is their very low atomic density (as low as 10^{20} cm^{-3}, as compared with 10^{23} cm^{-3} for typical condensed matter). This is obviously related to a very high porosity and high specific area. Although characterized by a shape (which is that of the vessel in which they were prepared), aerogels may easily be obtained with the same atomic density as gases at standard conditions. In this very open structure, practically all atoms are exposed to the ambient atmosphere. Other special properties include their extremely low thermal conductivity and very good textural and structural stability at high temperatures.

Inherent in the preparation processes of aerogels is control of their structure and morphology from the macroscopic level (preforming the material into monoliths, powders, lumps) down to the mesoscopic one (usually referred to as the porous structure, which is controlled by changing various parameters during preparation, such as pH, solvent, amount of water added for reaction) and finally to the microscopic level (complete atomic exposure).[69]

The homogeneity of the gels depends on the solubility of reagents in the solvent used, the sequence of addition of reactants, the temperature, and the pH. Network forming elements, such as Si, metals of principal groups, lanthanides, and early transition metals, must be used to obtain fairly homogeneous solids. The usual precursors which are readily available commercially for preparation of oxide aerogels are organic alkoxides, acetates, or acetylacetonates, as well as inorganic salts, such as chlorides. Among the classes of solvents, alcohols are largely used, but other solvents (benzene) may also be used for some alkoxides. The catalysts introduced in the polycondensation stage are volatile acids (acetic acid) or bases (ammonia).

The versatility of the sol−gel process is so extensive that the number of catalytic materials prepared as aerogels has increased rapidly. In Table 1, we update the list of aerogels prepared as potential catalysts or catalyst supports based on data reported in two very recent comprehensive reviews.[70] The method of preparing aerogel materials can easily be applied to obtain single-metal oxides customarily used as catalyst supports. As an example, preparation of thermoresistant, impurity-free alumina supports with high surface area and variable crystallinity[71−73] of very pure magnesium oxide,[74] of amorphous silicoaluminates,[75,76] and of uniform nanosize silica particles[77,78] has been reported. In addition, the sol−gel method was extended to preparation of multicomponent metal oxides. A detailed discussion of the preparative details may be found in Pajonk's review.[70] Synthesis is based on cogelation of suitable metal derivatives in appropriate organic solvents, using stoichiometric amounts of water and volatile acids and bases as catalysts. Supercritical drying is then conducted at the highest critical temperature of either the organic solvents or dispersing agents used. Materials with new properties could be prepared in this way. For example, incorporation of MoO_3 in alumina led to a modified structure of the alumina network, which preserves a high surface area and prevents segregation of MoO_3 even at high loading.[72] In binary oxidic systems, dispersion of one component in the matrix of the second oxide may either stabilize metastable crystalline phases (cubic ZrO_2 in ZrO_2-SiO_2 system[79]) or may prevent crystallization of the second oxide (niobia in $Nb_2O_5-Al_2O_3$[80]

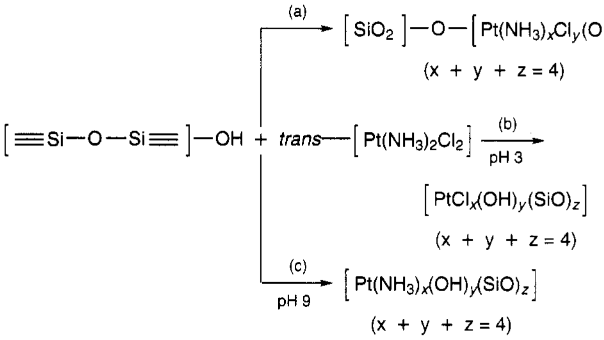
Table 1. Application of Aerogel Techniques for Preparation of Catalytic Materials

single oxides	ref(s)	single oxides	ref(s)
SiO_2	62,77,78	MgO	74
Al_2O_3	62,63,73	MoO_2	62
ZrO_2	62	NiO	62
TiO_2	62	V_2O_5	62,81
ThO_2	62	CuO	62
Cr_2O_3	62	PbO	62
Fe_2O_3	62	CeO_2	82
binary oxides	**ref(s)**	**binary oxides**	**ref(s)**
$NiO-SiO_2$	62	$V_2O_5-TiO_2$	81
$NiO-Al_2O_3$	62	$Nb_2O_5-Al_2O_3$	80
NiO−MgO	62	$SiO_2-Al_2O_3$	75,76
V_2O_5-MgO	62	$MoO_3-Al_2O_3$	72
$Cr_2O_3-Al_2O_3$	62	TiO_2-SiO_2	*a*
$PbO-Al_2O_3$	62,71	SiO_2-TiO_2	*b*
$PbO-ZrO_2$	71	TiO_2-CeO_2	82
$Fe_2O_3-Al_2O_3$	62	ZrO_2-SiO_2	79
$Fe_2O_3-SiO_2$	62	$CuO-SiO_2$	*c*
$CuO-Al_2O_3$	62		
ternary oxides	**ref**	**ternary oxides**	**ref**
$NiO-SiO_2-Al_2O_3$	62	$Fe_2O_3-NiO-Al_2O_3$	62
$NiO-Al_2O_3-MgO$	62	$Cr_2O_3-Al_2O_3-MgO$	62
$NiO-SiO_2-MgO$	62	$Cr_2O_3-Fe_2O_3-MgO$	62
$NiO-Fe_2O_3-Al_2O_3$	62	$Cr_2O_3-Fe_2O_3-Al_2O_3$	62
$NiO-V_2O_5-MgO$	62	$MoO_3-CoO-Al_2O_3$	73
$NiO-MgO-Al_2O_3$	62	$V_2O_5-TiO_2-SiO_2$	81
metal oxide	**ref**	**metal oxide**	**ref**
$Pt-SiO_2$	62	$Pd-SiO_2$	87,*d*
$Ni-SiO_2$	62	$Cu-ZrO_2$	62
$Ni-Al_2O_3$	62	$Cu-ZrO_2-Al_2O_3$	62
$Ni-SiO_2-Al_2O_3$	62	$Cu-ZnO-Al_2O_3$	62
$Ni-SiO_2-MgO$	62	$Rh-SiO_2-Al_2O_3$	76
$Cu-Al_2O_3$	62	$Rh-TiO_2-SiO_2$	*a*
$Cu-SiO_2$	62	Rh−MgO	91
CuO−MgO	62	$Rh-TiO_2$	91
$Ni-MoO_2$	62	$Ru-SiO_2$	90,89
$Pt-MoO_2$	62	$Ru-Al_2O_3$	89
$Pt-SiO_2$	92,*d*,*e*	$Pt-Sn-Al_2O_3$	*f*
$Pd-Al_2O_3$	62		

[a] Cauqui, M. A.; Calvino, J. J.; Cifredo, G.; Esquivias, L.; Rodriguez-Izquierdo, J. M. *Non-Cryst. Solids* **1992**, *147/148*, 758. [b] Ingo, G. M.; Dire, S.; Babonneau, F. *Appl. Surf. Sci.* **1993**, *70/71*, 230. [c] van der Grift, C. J. G.; Mulder, A.; Geus, J. W. *Coll. Surf.* **1991**, *53*, 223. [d] Lopez, T.; Moran, M.; Navarette, J.; Herrera, L.; Gomez, R. *J. Non-Cryst. Solids* **1992**, *147/148*, 753. [e] Lopez, T.; Romero, A.; Gomez, R. *J. Non-Cryst. Solids* **1991**, *127*, 105. [f] Gomez, R.; Bertin, V.; Ramirez, M. A.; Zamudio, T.; Bosch, P.; Schifter, I.; Lopez, T. *J. Non-Cryst. Solids* **1992**, *147/148*, 748.

and vanadia in $V_2O_5-TiO_2-Al_2O_3$[81]). Moreover, new compounds could be formed under mild conditions ($CeTiO_3$,[82] $AlNbO_4$[83]).

The reducing properties of most alcohols used either as solvents or dispersion media combined with the autoclave conditions required for supercritical drying results in the possibility of preparing in situ reduced metal catalysts on aerogel supports. This is achieved by cogelling precursors of easily reducible oxides (NiO, CuO) together with those of their carrier, eventually under a hydrogen atmosphere.[84] For platinic metal catalysts, the incorporation of the metal precursor (salts, inorganic complexes) during the gelation step results in additional interactions between terminal hydroxyls of the gel network and the metallic precursor and eventually in the incorporation of the latter into the gel structure. Lopez and co-workers[85-90] demonstrated in a series of papers that Pt, Pd, Ru, and Rh introduced as chlorides or chloro amines interact strongly in the coordination sphere with silanol groups of the fresh silica, e.g.



(5)

where process a is only a weak surface interaction, while processes b and c represent strong interactions with the bulk of the silica support.[91] The fact that the sol−gel method generates either structures like those shown above or of the type $[SiO_2]^{-OH}_{-[PdCl_xOH_x]}$[87] and Ru/SiO_2-OH[90] could explain the novel behavior of the catalysts, such as high selectivity in hydrogenation of acetylenics and high resistivity to coke deposition. However, Gonzalez[92] reports, on the basis of a TEM study of the catalyst prepared by this improved sol−gel method, that these catalysts are not always highly dispersed. Thus, it appears other explanations are necessary to account for the robust activity of these sol−gel catalysts and their ability to resist coke formation.

5. Crystallization

The method of crystallization has found wide applications in the preparation of homogeneous microporous solids, a class of monophase crystalline solids in which the active phase is distributed uniformly. They comprise the general class of materials designated as molecular sieves. In 1932, McBain[93] proposed this term to describe materials that exhibited selective adsorption both in terms of the size and the shape of the adsorbates. Since that time more than 200 molecular sieve structures have been discovered, and their organization has been made on the basis of both structure and elemental compositions. These microporous crystalline solids are structurally based on frameworks formed by linked TO_4 tetrahedra with each oxygen shared between two T elements.

One of the most important factors in the synthesis of molecular sieves is the chemical composition of the gel from which the crystalline products are separated. A wide range of organic and inorganic compounds have been used to modify the crystallization procedure. A simplified mechanism[94] depicted in Figure 3 shows the essential features of the steps involved. In addition to the gross composition and the reaction mixture, time and temperature also influence the structure of the final product. When the crystal growth is carried out in aqueous solution above or near 375 K, the conditions are designated as "hydrothermal"; this has proven to be the most efficient way thus far to produce these microporous materials.

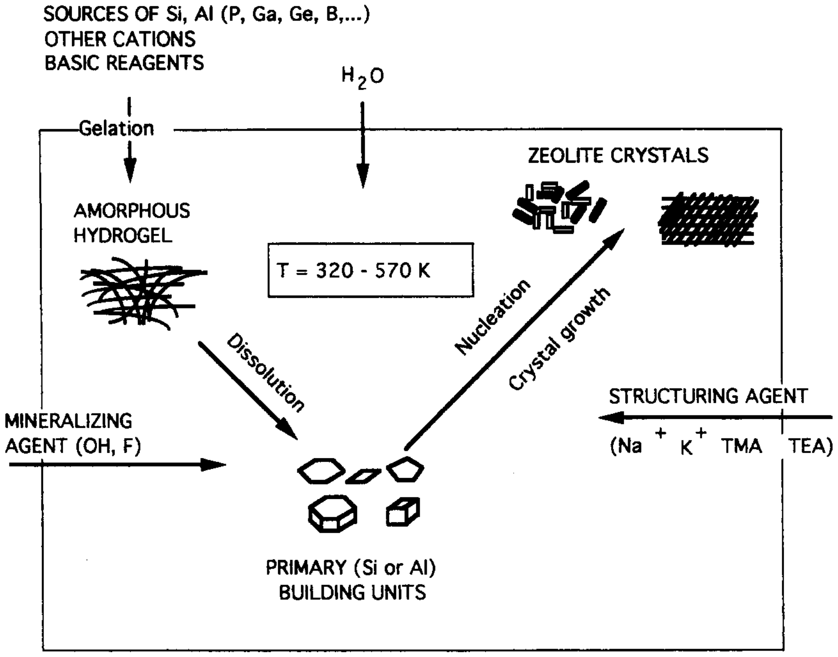


Figure 3. Simplified schematic of the steps involved during synthesis of molecular sieves.

Zeolites are distinguished from other molecular sieves on the basis that zeolites are a crystalline aluminosilicate with a framework based on a three-dimensional network of oxygen ions with Si^{4+} and Al^{3+} ions occupying the tetrahedral sites formed by the oxygens. The AlO_4 tetrahedra determine the framework charge which is balanced by cations occupying nonframework positions. Thus, a representative empirical formula for a zeolite is $M_{2/n}O\cdot Al_2O_3\cdot xSiO_2\cdot yH_2O$, where M represents the exchangeable cation (also including nonmetal and/or organic cations), n is its valence and x is a number equal to or greater than 2 because Al^{3+} does not occupy adjacent tetrahedral sites. Typical cations include alkali metals, alkaline earth cations, NH_4^+, H_3O^+ (H^+), tetramethylammonium (TMA), other nitrogen-containing organic cations, rare earth ions, and noble metal ions. The crystalline framework structure of zeolites contains voids and channels of discrete size. These may be divided into three major groups according to their pore/channel system. A listing based on the largest pore opening is given in Table 2.

Table 2. Classification of Zeolite Structures as a Function of the Number of TO_4 Units That Shape the Pore Opening

8 ring	10 ring	12 ring
bikitaite	dachiardite	beta
brewsterite	epistilbite	cancrinite
chabazite	ferrierite	faujasite (Type X, Y)
edingtonite	laumontite	gmelinite
erionite	stilbite	mazzite
gismondine	ZSM-5 (silicalite)	mordenite
heulandite	ZSM-11	offretite
levyne	ZSM-22 (theta-1)	omega
merlionite	ZSM-23	type L
natrolite	ZSM-48 (Eu-2)	ZSM-12
paulingite	ZSM-50 (Eu-1)	
phillipsite		
rho		
thomsonite		
TMA-E (AB)		
Type A, ZK-5		
yugawaralite		

The shape of the 8-membered oxygen rings varies from circular to puckered to elliptical. Straight chain molecules such as n-paraffins, olefins, and primary alcohols can be adsorbed by this group. The pore/channel systems of these zeolites also contain interconnecting "supercages" which are much larger than the connecting windows.

Almost all members of the 10-membered oxygen ring systems are synthetic. This framework structure contains 5-membered oxygen rings and thus are more siliceous than previously known zeolites. Dwyer and Jenkins[95] have considered them as "silicates" with framework substitution by small quantities of alumina. As in the case of the small pore zeolites, the shape and precise size of the 10-membered oxygen rings also varies from one structural type to another. Among the zeolites in this group, ZSM-5 and ZSM-11 have bidirectional intersecting channels. The H-form of these zeolites are very stable acidic catalysts. Furthermore, they have pores of uniform dimensions with no large supercages containing smaller size windows. Three factors are probably responsible for the successful industrial application of these zeolites: high silica to alumina ratios, geometrical constraint imposed by the 10-membered oxygen-ring-sized pores, and the absence of bottlenecks in their pore system which precludes the inclusion of large polynuclear hydrocarbons responsible for coking and irreversible deactivation.[96]

Zeolites containing dual pore systems have interconnecting channels of either 12- and 8-membered oxygen rings openings or 10- and 8-membered oxygen ring openings. Acidic zeolite catalysts in this class have a tendency to coke and deactivate readily because of their intersecting channels of different sizes. Large 12-membered oxygen ring openings or supercages deactivate more rapidly than medium or small pore materials during acid catalyzed reactions.

A typical zeolite synthesis involves mixing together alkali, sources of AlO_2^- and SiO_2, water, and other

Table 3. The Effects of Several Synthesis Variables on the Properties of the Final Products in Zeolite Crystallization

composition of reaction mixture	influence on crystallized products
SiO_2/Al_2O_3 ratio	framework composition
H_2O/SiO_2 ratio	rate and mechanism of crystallization
OH^-/SiO_2 ratio	molecular weight
inorganic cations/SiO_2 ratio	zeolite structure and cation distribution
organic additives/SiO_2 ratio	zeolite structure and content of framework Al^{3+}

Table 4. Influence of SiO_2/Al_2O_3 Ratio on the Physical Properties of Zeolites

high SiO_2/Al_2O_3 ratio	low SiO_2/Al_2O_3 ratio
improved acid resistance	increased hydrophilicity
improved thermal stability	high cation exchange capacity
increased hydrophobicity	
low affinity for polar adsorbents	
low cation exchange capacity	

components in appropriate proportions; the resulting gel is then subjected to elevated temperatures (generally less than 625 K). It is of interest to know what species are present at the beginning of the reaction. Aluminate and silicate solutions have been studied individually. Aluminate solutions contain only one type of ion at high pH; the tetrahedral $Al(OH)_4^-$ ion is the important species for normal zeolite synthesis.[97] When the pH moves toward neutral, other polymeric ions appear. Silicate ions at high pH contain a range of small silicate polymers formed by corner-sharing tetrahedral SiO_4 units. Rings and cages are the preferred form of silicate species. Depending on the temperature and composition, the optimum crystallization time can range from several hours to several weeks. During this time period, the system is in a highly disordered state with a higher entropy than its ordered counterpart, the crystallized zeolite product. Ostwald's rule of successive transformations generally governs the formation of the final product, but changes in the hydroxide ion concentration and/or the presence of certain anions (Cl^-, SO_4^{2-}, NO_3^-) can also play a factor. One can follow the course of a crystallization either by stopping the crystallization at various times and sampling the batch, by taking samples while the process is occurring, or by running the process in a series of identical crystallization vessels charged with the same batch of starting gel. The latter has been the most extensively used.

Zeolite synthesis, unfortunately, enjoys the designation of an art to the uninitiated. A major reason for this is that not only does each component of the reaction mixture contribute to the crystallization of a particular zeolite structure, but all of the components are interrelated. Thus, changing two components together can influence the final product in a way different from that achieved by varying components individually. Despite this, it is possible to enumerate some general guidelines as to the effects of individual components of the mixture. These are presented in Table 3 and discussed in more detail in the following text.

The SiO_2/Al_2O_3 ratio in the gel places a constraint on the framework composition. Table 4 presents the general effects of changing the ratio on the physical properties of the zeolite product. For catalytic applications such as cracking and isomerization, zeolites improve with increasing SiO_2/Al_2O_3 ratio. Resistance to acids and heat treatment are also improved in this manner. On the other hand, for either adsorption or ion exchange processes, a decrease in this ratio is favored because of the required increase in cationic content for charge neutralization.

The methodologies employed for changing the SiO_2/Al_2O_3 ratio in the gel phase can also be important in achieving exceptionally high SiO_2/Al_2O_3 ratios. Modification procedures include addition of organic additives, use of novel sources of silica such as H_2SiF_6, and addition of complexing agents for the aluminum.

The hydroxide ion concentration influences, among other things, the nature of the polymeric species present in the reaction mixture and the rate at which these species interconvert by hydrolysis. Increase in the hydroxide concentration accelerates crystal growth and shortens the induction period preceding crystal formation. One explanation for this is that it acts to facilitate transport of the silicate and aluminate species by an enhanced solubility of the reactants at higher pH. The reactants will nucleate and grow faster because of the increase in the collision frequency between the more concentrated precursor species in the solution phase.

In addition to serving as charge compensators, inorganic cations present in the reaction mixture often appear as the dominant factor which controls the zeolite structure obtained; they can influence crystal morphology, crystallinity, and yield.[97] The effect of the added cations is, indeed, complex and may be due to many factors. The presence of different cations (as well as amounts) will modify the pH of the mixture with crystallization time. Another possibility has been described as a template theory. An ion (or neutral species) is considered to be a template or crystal-directing agent if, upon its addition to the reaction mixture, crystallization is induced of a specific structure that would not have been formed in the absence of the template. The process has been analyzed as one in which the zeolite structure grows around the template; thus stabilizing certain pore structures or subunits. The theory is not only limited to explaining the effects of inorganic cations; it has been shown that neutral and ionic organic amines also follow a similar templating effect although other explanations have been suggested.

The water content of the starting mixture also plays an important role in determining the structure of the zeolitic product. Water has been proposed to interact strongly with cations present in solution and becomes itself a sort of template for structure control. The role played by water is reinforced by results obtained from systems in which the crystallizing medium was not aqueous.[98,99] Compared with the large number of structures formed in aqueous solvents, few zeolites have been found to crystallize from nonaqueous solvents. Solvents such as hexanol, propanol, glycol, sulfolane, and pyridine have been used.

Charge imbalance due to the number of silicon and aluminum ions in the framework of zeolites gives rise to active sites; they are classified as either conventional Lewis or Brønsted acids. Classical Brønsted and Lewis acid models are described by Brønsted acidity which is proton donating and Lewis acidity which is electron accepting acidity. The former occurs in the zeolites when the cations balancing the framework anionic charge are protons; the latter when an aluminum atom is trigonally coordinated resulting in an electronic deficiency, and thus it can accommodate an electron pair.

Zeolitic acid catalysts are produced when the cations present in the freshly synthesized material are replaced with protons. Difficulties associated with the process are (1) large organic quaternary amine cations which are used in common synthesis routes today are difficult to remove from the pore system; (2) several exchanges are generally needed; and (3) direct proton exchange using acids results in leaching of aluminum ions from the framework.

Ion exchange is normally accomplished using an aqueous ammonium salt, and the resulting material is calcined to produce the acid form.[100-107] Direct treatment with HCl can also be used.[100,103-105,107] It has been shown that the activation method to introduce acidity also can induce variation in the reactive properties of the activated catalysts.[108] In summary, three major factors influence the activation process for the final acid catalysts: (1) the type of exchange treatment; (2) the degree of ion exchange; and (3) the condition of calcination subsequent to the exchange.

More than 10 years ago a new class of microporous materials became important in both industrial and research laboratories.[109] They are known as AlPOs, SAPOs, MeAPOs, and ElAPOs (El = As, B, Be, Ga, Ge, Li, Ti). They are derived by isomorphous substitution of $AlPO_4$. More than 27 different structures have been found, and 15 elements other than Al and P with oxidation states ranging from +1 to +5 have been incorporated into the $AlPO_4$ framework.

The synthesis of this wide scope of materials is characterized by[109,110] mildly acidic to mildly basic slurries (pH 3−10), narrow P/Al (0.8−1.7) composition, the common use of amines or alkylammonium ions as templating agents, a synthesis success (yield/performance) strongly dependent on source of reactants and stirring and aging of gel, and a high degree of isomorphous substitution during synthesis.

The net charge on the $AlPO_4$ molecular sieves is zero because the framework AlO_2^- and PO_2^+ units exist in equal amounts in their structure. Thus, the AlPOs have no ion exchange capacity; however, they do exhibit a reasonable attraction toward water due to the polar nature of the Al−O−P structure.

Recently, the first molecular sieve with rings having greater than 12 T atoms was synthesized.[111] The so-called VPI-5 is a family of aluminophosphates based molecular sieves possessing the same three dimensional topology. The extra-large pores of VPI-5 contain unidimensional channels circumscribed by rings which have 18 T atoms and possess free diameters of approximately 12 Å. While this material is interesting from the standpoint of its structure, its applications to catalysis have been limited. One reason is its hydrophobicity. Modification of acidity is accomplished through various dealumination techniques and/or doping with silicon.

B. Solid–Solid Blending

One of the most important requirements in the preparation of single metallic or multimetallic oxide catalysts is obtaining a good interdispersion of different phases and components which constitute the catalyst. Its importance arises in order to achieve the desired spatial distribution of the components for use in catalytic reactions where selectivity depends on the diffusion of the reactants. In an attempt to improve the homogeneity of the catalysts at the molecular or atomic scale, different procedures were developed. A common characteristic of these methods is the use, separately or combined, of both chemical and physical factors in order to control the global chemical reaction and to achieve a state of intimate interdispersion and mixing of either reagents or of reaction products.

Various methods based on solid−solid blending are frequently used for the preparation of mixed oxide catalysts; some were "borrowed" by the catalytic community from ceramic manufacturers.

In the high-temperature ceramic method, the mixed-oxide phase results from heating intimately mixed powders at temperatures high enough to allow interdiffusion and solid state reactions. The method has the advantage of the extreme simplicity, and its use is essential for preparing mixed oxides, such as perovskites,[112] with special morphologies such as single crystals or thin layers. A major shortcoming of the ceramic method is the lack of homogeneity of the materials prepared, because the solid state reaction between the precursor oxides occurs with very slow rates. The high temperatures (1300 K or above) required to complete solid state reactions between oxides lead to a drastic decrease in surface area of the resulting material by sintering. This severely limits the use of the ceramic method in preparation of catalysts designed for most low temperature processes. To overcome this problem, precursor compounds, such as carbonates and oxalates, that decompose at lower temperature, have been used instead of the corresponding oxides. Another strategy has been proposed and tested.

The method of temperature-programmed synthesis was used successfully to prepare carbides and nitrides with high surface area starting from precursors with very low specific surface area.[113] As shown by the schemes in Figure 4, the starting material was WO_3. This was converted to β-W_2N by using ammonia as the reducing gas and a very slow temperature ramp (ca. 0.10 K s^{-1}). In a second step, two modifications of tungsten carbide were prepared by carburizing either WO_3 or β-W_2N with a CH_4:H_2 = 4:1 mixture. The key to this method is that the temperature must be increased very slowly during nitridation or carburization, in order to preserve the topotactic character of transformation;[1] this leads to a porous solid (either tungsten nitride or carbide) with specific surface area in the range of 100−200

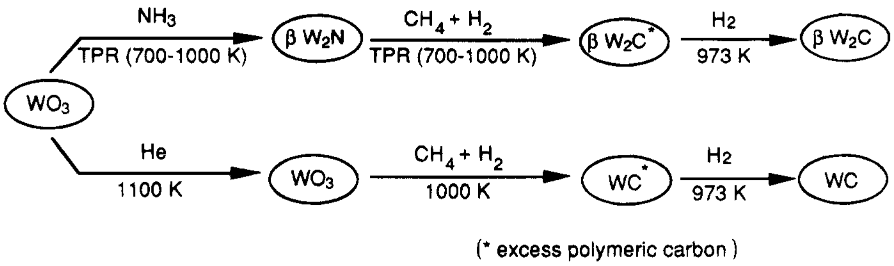


Figure 4. Scheme for producing tungsten carbides from tungsten oxide using temperature-programmed procedures.

$m^2\ g^{-1}$. The catalytic materials obtained, if devoid of excess polymeric carbon, are very active for reactions of hydrogenolysis and dehydrogenation of alkanes and alcohols and hydrogenation of alkenes, reactions that also occur on group VIII metals.[114]

The ceramic method finds application in the preparation of low surface area catalysts (0.5–10 $m^2\ g^{-1}$) which must resist deactivation in reactions at high temperatures. An interesting application of this method in preparation of oxide systems with valence-controlled dopants was described by Klier.[35] In the oxidative coupling of methane, ZnO is a low activity catalyst, but its reactivity is controlled by oxygen vacancies which can be generated by doping with lower valence ions, such as Cu^+. On the other hand, introduction of a redox Lewis acid such as Fe^{3+} is expected to change the reaction mechanism by oxidizing the methyl radicals to formaldehyde. Double doping of ZnO with Cu^+/Cu^{2+} and Fe^{2+}/Fe^{3+} redox couples was beneficial: Cu^+ acted as an oxygen activator for ZnO and Fe^{3+} as a selectivity switch to formaldehyde.[115] The doped ZnO catalyst was prepared by the ceramic method. At the high temperature employed, substitutional $Cu^+{}_{Zn}$ and $Fe^{3+}{}_{Zn}$ ions diffuse together in the ZnO lattice and enrich the surface region of the catalyst. The two substitute ions which were mutually attracted by Coulombic forces as Cu^+ and Fe^{3+}, represent, respectively, a negative and a positive charge with respect to the Zn^{2+} lattice.

In an attempt to obtain homogeneously uniform solids, avoiding the imperfections of the coprecipitation method or the severe heat treatments of the ceramic method, several other procedures were developed. The homogeneity of the solid product depends on the homogeneity of initial reagents. One of the simplest ways to obtain a homogeneous distribution of cations is to have them in solution. In some instances, the final solid product may be obtained without very severe heating, simply by removing the solvent. Different methods based on liquid-to-solid transformations were explored; they differ by the way in which the solvent is removed.

The simplest method is that of dry evaporation of a homogeneous solution that contains the precursor salts. This technique resembles the ceramic method because it may result in a nonhomogeneous solid depending on the crystallization rates of the various components. The homogeneity of the original solution is best conserved, for example, by increasing the rate of evaporation of the liquid. In the spray-drying technique, a solution is dispersed as fine droplets in a hot chamber. Very fine particles are formed and dried quickly, and then the product is collected as a powder.

A related method is that of freeze-drying in which the solution containing the desired decomposable compounds is sprayed into liquid nitrogen. In this way, very small particles are formed by rapid freezing, and the homogeneity of the initial solution is preserved. Removing the solvent by vacuum drying has a similar effect. This procedure may be used to dry solids with low melting temperatures and in many instances to preserve their amorphous or glassy character. These last techniques were used for the preparation of mixed oxides with perovskite structures and surface areas in the range of 10–50 $m^2\ g^{-1}$.[116–118]

C. Liquid–Solid Blending

Many commercial catalysts are manufactured by the co-mulling technique, a technique "borrowed" from ceramics. This procedure consists of blending a powder of dry aluminum hydroxide with a small amount of water, which may also contain other precursors of active ingredients of the catalyst, and a peptizing agent. A homogeneous paste is formed by kneading which is further extruded; the extrudates are dried and calcined. Extrusion permits production of catalysts and supports with smaller dimensions and at lower cost than pelleting.[119]

Extrusion has been used for manufacturing of ceramic materials, but development of the technology has remained fairly stagnant because the approach has been almost always empirical. Extrudable pastes are two-component systems that contain a particulate phase (a powder) and a continuous phase (a liquid). The selection of these two phases is critical to the success of the process, which depends on the rheology of the paste; it must have high viscosity at low shear rates and low viscosity at high shear rates.[120] In spite of its importance for large-scale preparation of catalysts, only a few papers addressed the problem from a theoretical viewpoint.[120–122] Empirical contributions have come from the field of ceramic materials science.[123] Unger[124,125] compared various commercial aluminas in relation to the manufacturing of porous supports by extrusion. Jiratova[119] showed that the effects of different peptizing acids on the properties of the extrudates can be generalized using the Hammet acidity function of the peptizing solution. Luck[126] used a battery of spectroscopic methods to compare $NiO-MoO_3-Al_2O_3$ hydrotreating catalysts prepared by kneading and by conventional impregnation.

III. Solid Transformations

A number of different procedures are used to form catalytic materials that do not fall into either the "blending" or the "mounting" classes. The common element that perhaps best describes these procedures is the transformation of a solid phase either by physical or chemical processes. In both cases, the preparation of unsupported metals and alloys as catalysts, either on the industrial or on the laboratory scale, is conditioned by the ability to stabilize metals in a physical form characterized by a large surface area.

A. Epitaxial Metallic Films

Massive metals, either polycrystalline or in the form of thin films and single crystals have limited applications as practical catalysts, while they do serve as excellent model systems in laboratory studies. Recent studies on surface catalytic reactions on thin expitaxial films approximately one monatomic layer thick formed on particular metal substrates show that the catalytic reactivity of the surface for a particular chemical reaction may increase significantly.[127,128] Thus, by using thin film techniques an almost limitless range of model surfaces, with their distinct surface chemistry, can be devised.

Epitaxy is a term that refers to the oriented growth of one material, the overgrowth, on a crystalline substrate. Those planes and directions which give the best lattice fit generally determine the orientation of the film with respect to the substrate. Misfit that occurs produces strain, which, if large enough, may generate line defects called misfit dislocations at the interface between the film and the substrate. These dislocations tend to reduce the misfit strain.

The processes that are involved in forming an epitaxial overgrowth may involve the solid, liquid, and vapor state while the growth of solid phases as alloys is controlled by interfacial relationships. In the liquid state, epitaxial overgrowth can be formed by electrodeposition or by a process called liquid phase epitaxy (LPE), whereby a saturated solution plates out a material on a particular solid substrate. Vapor phase methods are probably the most common and include (1) vacuum evaporation from a hot source onto a colder substrate (molecular beam epitaxy, MBE), (2) chemical vapor deposition (CVD), which involves surface chemical reactions of gases at pressures near atmospheric (e.g., thermal decomposition of a gas on a hot substrate or polymerization of monomers), and (3) ion sputtering processes whereby ions produced in a gas discharge (or by other gaseous ionization methods) are accelerated toward a target. The subsequent interaction by momentum interchange results in the emission of atoms or molecules from the target material which then are permitted to strike a substrate on which the film of interest grows.

The properties of epitaxial films can be made to vary widely because of the high reactivity of individual atoms and molecules. Thus, in combining the atoms to form a thin film, numerous physical and chemical processes may be involved, thereby making possible an almost limitless variety of properties, e.g., microstructure (i.e., defect content), orientation, composition, and topography. This result is especially true for very thin films. In this case, their physical, chemical, and mechanical properties may be widely different from those of either the bulk material or the substrate.

The formation of a thin film by any of the experimental methods mentioned is not a simple process. Atoms or molecules which are incident on a surface may either diffuse over the surface, diffuse into the bulk of the substrate, or be desorbed. In typical cases, one or more of these processes dominates the film formation process.

B. Unsupported Bulk Metals

The preparation and characterization of unsupported metal catalysts was recently reviewed;[129] platinum group metals are the widest used because of their high activity. A list, with examples, includes the Pt–Rh wire gauze used for oxidation of ammonia, the Pd–Au alloy wires used for selective hydrogenation of hydrocarbons, the Pt–Rh gauze used as a catalyst in the synthesis of hydrogen cyanide from methane and ammonia, and the wire and granular silver catalyst used for selective oxidation of methanol to formaldehyde. Palladium membranes have found application as a hydrogen permeable catalyst which integrates a hydrogenation and a dehydrogenation reaction in a unique catalytic reactor.[130,131] The use of an inorganic oxide "guard" phase (a layer of titania) was found to be effective in preventing the palladium surface from rearrangement under the action of temperature and reaction mixture.[130]

Preparation of bulk metal catalysts in the form of wires, foils, gauzes is fairly simple. Introduction of a second metal component was sometimes used as a practical means to vary systematically the properties of the resulting system.[132] Bulk bimetallic catalysts and alloys play a major role in fundamental research where the catalytic influence of the second metal component is studied. Recent results on the growth mode of evaporated bimetallic films (Pd–W, Pd–Ta[133–135]) and on their catalytic properties (Pt–Re[136]) demonstrate that bimetallic systems are catalytically interesting because of both geometrical and electronic effects.[137]

Methods to prepare alloys in the powder form use, for example, reduction of mixtures of either salts (chlorides, nitrides, carbonates) or hydroxides of the metals in question. The reducing medium is usually hydrogen, and the homogeneity of the alloy is ensured by either physically mixing the salts or calcining the hydroxides before reduction. Obtaining a high surface area is possible by keeping the reduction temperature as low as possible. The use of liquid media (either aqueous or nonaqueous) for reduction, such as hydrazine, formaldehyde, and sodium borohydride solutions might be preferred because of the lower temperature needed.

Metals can also be prepared in small-particle skeletal forms and used in either fixed-bed or slurry operating reactors. In this state their preferred morphology would consist of small particles, more or less separated from one another, and protected against sintering by an oxide stabilizer. The principle of alloying with aluminum, which is later selectively dissolved in very alkaline solutions, forms the basis of preparing Raney-type catalysts and has been applied to several metals, such as Ni, Co, Cu, Fe, Ag, and Re. However, the use of Raney-type catalysts is often limited by their propensity for self-heating and self-ignition in air, which is determined by the presence of a large amount of active hydrogen dissolved in the highly dispersed, lattice distorted, active metal.[138] The stability of Raney Ni catalysts can be increased by mild surface oxidation[139] which leads to formation of a protective film of nonstoichiometric nickel oxide.

Progress in the preparation of Raney-type catalysts was made by the technology of making activated metal supports and metal catalysts, using any configuration into which metals can be fabricated (pellets, sheets, foils, single crystals, etc.). The method entails the steps of high-temperature deposition and diffusion of volatile metal compounds (halides) on the base of a metal substrate, followed by high-temperature diffusion to form an intermetallic compound on the base metal surface. Selective removal of the diffused metal leaves behind the base metal with a depleted lattice and a high and active surface area. The Baldi–Damiani technology[140] provides a means to synthesize metal and support in any size, shape, or form. Because these supports are thermally conductive and can be made in almost any configuration, the Baldi–Damiani activated metals should find application in highly exothermic reactions and in processes in which significant pressure drops must be avoided.

C. Amorphous Alloys

A technique for producing metallic alloys by rapidly quenching melts has attracted the attention of metallurgists, physicists, and recently, catalytic chemists[141–144] because of the exceptional properties of the materials obtained. They have neither long-range order nor complete amorphous character. Materials prepared by metal quenching methods are referred to as amorphous metal alloys or metallic glasses. These cognomers underscore the fact that such materials are never pure metals, but alloys with a rigid structure and short-range ordering. Several reviews appeared recently on their catalytic applications.[145,146] Although many elements of the periodic table can form a variety of alloys with glassy structure, only certain compositions have been studied for their catalytic properties. One groups is that of metal–metalloid alloys comprised of a late transition metal (Ni, Co, Fe, Pd, Au, about 80 atom percent) and a metalloid (B, C, Si, Ge, P) which contributes to the lowering of the melting point. A second group is that of metal–metal glasses with typically 1:1 composition (e.g., Ni–Ti, Cu–Ti, Ni–Al, Pd–Zr, Cu–Zr, Ni–Nb, Ti–Be, Ca–Mg).

Obtaining noncrystalline metal alloys with a metastable structure requires cooling of the melt at a rate high enough that crystallization does not occur. In the melt-spinning technique, this is achieved by rapidly increasing the melt surface area and transforming it into ribbons or tapes. Most catalytic studies have concentrated on ribbon samples prepared by this technique.[144,147,148] In many cases, the as-prepared alloys have low surface area and minimal catalytic activity, so that activation of the catalyst surface is needed. Activation of amorphous metal catalysts uses procedures that are common to those of traditional metal catalysts, such as reduction in hydrogen at elevated temperatures and oxidation by acid etching followed by reduction with hydrogen. Activation by a leaching procedure may result in the formation of a rough, Raney-type porous surface, as was revealed by electron microscopy studies of amorphous alloys containing Zr.[149] Another route to prepare highly active catalysts from pretreated metallic glasses consists of selective oxidization of the more electropositive metal, which results, after reduction, in finely dispersed transition metal particles embedded within a partially crystalline oxide matrix.[150]

Other techniques, such as vapor and sputter deposition, flash evaporation, and chemical reduction, were used to produce amorphous alloys. A promising alternative was recently developed to produce amorphous metal catalysts with high surface area. In the spark erosion technique, a repetitive spark is maintained between two electrodes of the material to be quenched, while it is immersed in an organic dielectric fluid.[151,152] At the extremely high cooling rates provided by this method, amorphous metallic powders were prepared that were found to be active for methanol (Cu–Zr, Cu–Zn, Cu–Zn–Al) or Fischer–Tropsch (Fe–B) synthesis. This technique overcomes two major shortcomings of amorphous ribbons when used as catalysts: their low surface area and their surface nonhomogeneity.

The use of metallic glasses in catalytic applications is limited to low temperatures because the amorphous state is thermodynamically unstable and tends to crystallize. Once exposed to temperatures above their crystallization point, the amorphous character may be lost and the catalytic activity may be drastically changed. However, there are indications that a small amount of crystallinity seems to improve the properties of metallic glasses.[153,154] The use of an organic liquid as a sparkling medium for the powders obtained by the spark erosion method leads to the formation of a carbon matrix of high surface area that has a stabilizing effect for dispersed amorphous metallic particles.[151,152]

D. Colloidal Metals

The ultimate dispersion state in which metals can be prepared without major alteration of their properties is that of metal sols. Colloidal metals have found numerous applications in catalysis, especially for catalysis in solutions, and are also used for the preparation of supported metal catalysts.[155] Colloidal metal particles prepared by growth from molecular precursors are usually small and exhibit a narrow size distribution. The chemical reaction most suitable for obtaining colloidal metals by this method is the reduction of metallic ions. Many reducing agents have been used, the most popular being formaldehyde, alcohol, carbon monoxide, hydrogen peroxide, and hydrazine. Metallic particles dispersed in water carry electric charges and must be protected against aggregation. The presence of electrolytes destabilizes such colloidal dispersions and addition of a synthetic polymer, both in soluble and insoluble form, protects such dispersions from coagulation. In practice, reduction can either precede or follow the interaction of the colloid with the polymer. The simplest method of preparation is refluxing of alcoholic solutions of metal salts in the presence of the protective polymer. Bimetallic systems can be prepared by the same procedure from solutions containing two metal compounds.[156,157] A list of metals which have been prepared and characterized in colloidal solutions includes Pt, Pd, Ru, Rh, Os, Au, Ag, and bimetallic systems such as Pd/Pt.[158]

The unsupported metallic catalysts derived from different transformation routes do serve to produce practical materials suitable for use in industrial processes. However, "mounted" catalysts offer special advantages as well as disadvantages as will be discussed in the following sections. Our focus is pragmatic; we emphasize the methodologies and the underlying physicochemical processes that determine the transport and "mounting" of catalytic elements from one phase onto another.

IV. Two-Dimensional Chemistry

Multiphase catalysts are nonuniform solids at the molecular or crystalline level and usually consist of an active phase dispersed on a carrier; the catalytic reaction takes place at the internal surface (in the pores) of the catalyst.

Preshaped supports are attractive because their texture, which can be regulated in advance, is transmitted almost unchanged to the final catalyst. However, after introduction of the catalytic component onto preshaped supports, care must be taken that dispersion and macroscopic distribution of the catalytic components is not altered during subsequent preparation steps. With powdered supports, the intimate mixing of the catalytic ingredients is easily realized in the first step of preparation, but all additional operations in which the catalyst grains are transformed into their required shape and porosity are rendered more difficulty by the presence of the catalytic materials.

Catalysts prepared on preshaped supports can have nonuniformly distributed activity throughout their structure. For certain processes, this might be undesired, but in general, a nonuniform distribution improves performance especially when deactivation processes occur at the pore mouth. A number of studies have explored the relationship between the optimal catalyst activity profile in catalyst pellets and catalytic performance (activity and selectivity).

Research in catalyst preparation seeks for a better understanding of the factors that control the distribution of the active components mounted on preshaped supports. Methods to regulate the distribution of the catalyst in impregnated pellets have been periodically reviewed.[159-164] One published recently[164] emphasizes the possibility to design catalysts with optimum activity profiles for particular processes and reactor conditions.

Virtually any solid which has a surface area of the order of 10^1-10^2 m^2 g^{-1} can be used as a support. Table 5 lists typical examples or inorganic and organic support materials. Chemical modification of polymeric supports can be achieved by bonding ligands followed by fixation of metals on the functionalized polymers. Most polymeric supports can be used at high pressures and are resistant to sudden changes of solvent polarity; they also have the advantage of inertness over wide pH ranges, while inorganic oxides dissolve in highly acidic or basic environments. However, polymer swelling in the presence of different solvents makes control of diffusional procedures difficult, and their degradation at temperatures of about 420 K is their most serious drawback as a support. Consequently, the use of polymer-attached catalysts[155] has remained a subject of academic interest rather than an active field of application.

Table 5. Materials Used as Supports in Catalyst Synthesis

inorganic	organic
alumina	polystyrene
silica	polymethacrylate
titania	polybutadiene
magnesia	polyvinyls
active carbon	polyamines
zeolites	polyamino acids
molecular sieves	cellulose
porous glass and ceramics	silicon resins
natural clays	cross-linked dextrans

Preference given to metal oxides and to a lesser extent active carbon as supports for catalyst manufacturing is a consequence not only of their thermal and chemical stability but also of our ability to prepare these materials with high surface areas. In addition, significant progress in their characterization has made them versatile and at least comparable in performance to that shown by functionalized organic polymers.[165,166]

The heterogenization of homogeneous catalysts was an attractive area of research in the 1970s.[167-169] It was extensively used for preparation of model systems by immobilization of either inorganic[170] or organometallic compounds[171] and by attaching metallic clusters[172] on either inorganic or polymeric supports, very often by means of organic solvents and generally after an appropriate surface functionalization.

The manner in which the active component of the catalyst is introduced onto a support as well as the nature and strength of precursor–support interactions have a significant influence on the properties of the active component in the final catalyst. A general scheme for the classification of the different roles the support can play with respect to the introduction of metal cations during catalyst preparation was proposed by Che.[173,174] With minor modifications, the same scheme may be generalized to any type of active precursor introduced from solution.

The following precursor/support interactions may be distinguished: crystallization of precursor in the pore-filling solution during solvent evaporation (the support pores act as a microrecipient; the chemical identity of immobilized species does not change); electrostatic interaction, followed by either ion exchange or electrostatic adsorption (the support surface acts as an outer-sphere macroion; the inner sphere of the immobilized species is not changed); grafting of isolated species by ligand exchange with surface hydroxyl groups (the support acts as a ligand;

the coordination sphere of the immobilized species is changed); formation of new chemical compounds at the interface (the support acts as a reactant; the identity of immobilized species is completely altered).

The two-dimensional chemistry at the interface formed between the support and the catalytic ingredients, therefore, plays a major role in determining the success of catalyst production and reproduction. This chemistry falls into the domains of colloidal events generated by pH-dependent surface charge and coordinative events correlated with the intrinsic reactivity of surface groups.[175]

A. Mounting Dissolved Precursors from Aqueous Phase

A major route for preparation of catalytic materials and catalysts involves the use of aqueous media where surface hydroxyls on oxides are important as proton acceptor/proton donor sites as well as surface ligands. Precursors are introduced onto the support either by simple impregnation and drying (in absence of support–precursor interaction) or by homogeneous deposition–precipitation, ion exchange, and specific adsorption (when support–precursors interact with various degrees of intensity). The specific reactivity of surface hydroxyls on oxides is also important for either the deposition or the decomposition of active precursors introduced from either the gas phase or from organic solvents. In all cases, one deals with formation of ill-defined surface complexes whose stoichiometry is generally not known. They may have some properties in common with known compounds, but, more likely, they find no analogs from classical patterns in three-dimensional chemistry. It is, therefore, not surprising to see that the emergence of better characterization techniques has lead to revision of older explanations for the interaction mechanisms associated with the preparation schemes. An intrinsic benefit has been the development of new, nontraditional synthesis routes.

Due to the inherent importance of hydroxyl groups on oxides, a more lengthy discussion of them is relevant.

Metal oxide surfaces are mainly composed of oxygen atoms and hydroxyl groups; exposed metal atoms may become important but only after dehydration at elevated temperatures. Although surface reconstruction has been observed, existing experimental techniques cannot determine with certainty where the atoms actually are on the surface; ideal unrelaxed models for surface geometry are still accepted as good approximations for most oxide surfaces to interpret the spectroscopic[176–178] and thermodynamic[179] properties of surface groups on oxides.

Although there has been a significant increase in both experimental and theoretical studies of metal–oxide[180–182] and oxide–oxide[183–186] interfaces, the factors which can be used to control catalyst preparation in real systems are still obscure. New experimental data has made necessary the introduction of new concepts concerning the structure of supported catalysts. Thus, the term *chemical glue* was introduced to describe the stabilizing action of unreduced or partly reduced metal ions acting as grafting sites at the interface between small metal particles and conventional oxide supports.[180,181,187] Similarly, the concept of *oxide monolayers*, which could not be found in the literature before 1980, is now used to describe the state of monomolecular dispersion of surface oxo species, with quite unusual properties that can be stabilized below monolayer threshold in many oxide–oxide systems. In many applications, supported oxides are most efficiently used when present as thin layers over the surface of another oxide; in the monomolecular dispersed state, the deposited overlayer is maximally influenced by the support.[188]

Parallel observations of the influence of the host oxide has been observed. So-called surface oxide–surface interaction (SOSI) and strong metal–support interaction (SMSI) are cognomers which provide names but do not contribute to our understanding of how to produce them during catalyst preparation. Efforts made to obtain more information on the nature of the interaction between the dispersed phases and the corresponding oxide supports point to the fact that the concentration and reactivity of hydroxyl groups at oxide surfaces are important properties related to the preparation of catalysts dispersed on inorganic oxides.

The behavior of hydroxyl groups at the oxide surface depends strongly on the composition of the oxide and the local chemical environment. Describing the surface coordination around a metal ion as $M^{z+}O_m(OH)_n$ the Brønsted acid strength of –OH bonds increases as m increases and also as z increases. The spatial heterogeneity of oxide surfaces leaves oxygen atoms exposed on the surface which differ from each other by the number and type of surrounding metal cations. These differences in the configuration determine the occurrence of various types of surface hydroxyls. On partially dehydrated surfaces, they have various acid/base character,[189] and this is well documented by different experimental methods, including IR spectroscopy.

Despite the existing evidence that oxide surfaces have hydroxyl groups of different acid strengths, the effects of intrinsic heterogeneity of acid/base properties at the oxide/aqueous solution interface were only recently examined from both a theoretical[190–194] and experimental[195–197] point of view. The most important result for the preparation of oxide supported catalysts from aqueous solutions is the recognition that at the solid/solution interface of (hydr)oxides, various types of surface groups exist, each reacting according to their own proton affinity constant (K). Hiemstra et al.[198,199] developed a multisite surface complexation model for estimation of log K values for various types (single, double, triple metal-coordinated) surface groups of (hydr)oxides. Proton adsorption reaction can be, in principle, considered as two-step processes:

$$[(M^{v})_n{-}O]^{\Sigma v-2} + H^+ \Leftrightarrow [(M^{v})_n{-}OH]^{\Sigma v-1} \qquad K_i^{\Sigma v-2} \quad (6)$$

$$[(M^{v})_n{-}OH]^{\Sigma v-1} + H^+ \Leftrightarrow [(M^{v})_n{-}OH_2]^{\Sigma v} \qquad K_i^{\Sigma v-1} \quad (7)$$

of proton binding by oxo or hydroxo groups, forming

$-OH$ and $-OH_2$ species at the surface. A theoretical analysis showed that the intrinsic affinity constants of various types of surface groups depend on the local configuration of the surface (number of surrounding cations, n, and their effective bond valence, v). Also, the difference between successive $\log K_i$ values for proton binding on $-O$ and $-OH$ groups with the same surface configuration is so high (about 14 log K units) that only one protonation step can be observed for each surface configuration within the normal pH range (3–11). Thus, the proton binding curve determined by potentiometric titration can be regarded as a multiple adsorption isotherm, consisting of several Langmuir isotherms, one for each geometrically determined category of surface sites.

Machesky and Jacobs[200,201] obtained by titration calorimetry the experimental evidence that proton adsorption enthalpies on alumina varies with pH and ionic strength. They concluded that two or three distinct types of proton binding sites exist at the alumina/solution interface. Using a more elaborate technique, Schulthess and Sparks[202] measured proton binding isotherms on alumina which revealed plateaus and inflections, in contrast with the featureless character of previous reports. Recently, Contescu and Schwarz used deconvolution procedures based on the Rudzinski–Jagiello (RJ) approximation[203] and calculated the proton affinity distribution of surface sites on alumina[195] and other oxidic systems[204] from smoothed potentiometric titration data.

In Figure 5, the experimental proton binding isotherm on alumina is superimposed onto the calculated proton affinity distribution, $f(\log K)$. It is seen that three or four categories of surface sites contribute to proton binding and surface charge development between pH 3 and 11. They were identified[195–197] with types I (terminal), II (bridging), and III (triple coordinated) surface hydroxyls in accordance with the structural model advanced by Knözinger and Ratnasamy.[205] These surface groups react specifically with solution protons, depending on their $\log K_i$ and the solution pH.

$$[\mathrm{Al^{VI}{-}O{-}Al^{IV}}]^{0.75-} + \mathrm{H^+} \leftrightarrow [\mathrm{Al^{VI}{-}OH{-}Al^{IV}}]^{0.25+} \qquad \log K_{\text{II-a}} \approx 4.1 \quad (8)$$

$$[\mathrm{Al^{IV}{-}OH}]^{0.25-} + \mathrm{H^+} \leftrightarrow [\mathrm{Al^{IV}{-}OH_2}]^{0.75+} \qquad \log K_{\text{I-a}} \approx 6.8 \quad (9)$$

$$[\mathrm{Al^{VI}{-}OH}]^{0.5-} + \mathrm{H^+} \leftrightarrow [\mathrm{Al^{VI}{-}OH_2}]^{0.5+} \qquad \log K_{\text{I-b}} \approx 9.8 \quad (10)$$

Other proton binding equilibria on alumina cannot be observed within the normal pH range:

$$[\mathrm{Al^{VI}{-}OH{-}Al^{VI}}]^{0} + \mathrm{H^+} \leftrightarrow [\mathrm{Al^{VI}{-}OH_2{-}Al^{VI}}]^{1+} \qquad \log K_{\text{II-b1}} \approx -2 \quad (11)$$

$$[(\mathrm{Al^{VI}})_3{-}\mathrm{O}]^{0.5-} + \mathrm{H^+} \leftrightarrow [(\mathrm{Al^{VI}})_3{-}\mathrm{OH}]^{0.5+} \qquad \log K_{\text{III}} \approx 2.5 \quad (12)$$

$$[\mathrm{Al^{VI}{-}O{-}Al^{VI}}]^{1-} + \mathrm{H^+} \leftrightarrow [\mathrm{Al^{VI}{-}OH{-}Al^{VI}}]^{0} \qquad \log K_{\text{II-b2}} \approx 12.5 \quad (13)$$

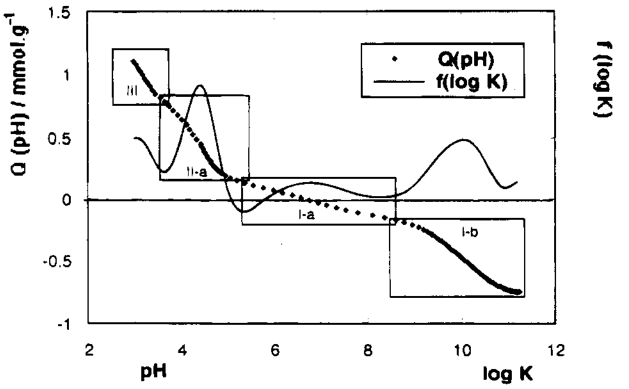


Figure 5. Experimental proton binding isotherm from potentiometric titration of γ-Al_2O_3 and calculated proton affinity distribution.

A direct consequence is that at any pH, the oxide surface exhibits sites which carry positive charges (if their $\log K >$ pH) and sites with negative charges (with $\log K <$ pH); they are disposed in regular arrays on different crystal planes at the oxide surface. Another consequence is that, even at the pH corresponding to an apparent point of zero charge (PZC), some of the above sites may still be charged. For very heterogeneous surfaces, the concept of PZC must be more carefully considered for in reality it is a global surface property rather than a thermodynamically meaningful constant.[206]

1. Impregnation

The mounting of dissolved aqueous precursors on oxide supports is generally accomplished by the so-called *impregnation* method. This term denotes a procedure whereby a certain volume of solution containing the precursor of the active element of the catalyst is contacted with the solid support. If the volume of solution either equals or is less than the pore volume of the support, the technique is referred to as incipient wetness.

When the interaction strength of the active precursor in solution with the support is weak, the method of incipient wetness impregnation followed by drying may be used to apply high loadings of precursors; the maximum loading is limited by the solubility of the precursor in the pore filling solution. On the other hand, increasing the weight loading requires higher concentrations which, for reagents such as $Ni(NO_3)_2$, results in lower solution pH and, in turn, may cause support disruption and substitution of ions into the support lattice.[207] However, in the absence of sufficiently strong interactions, the drying step usually results in severe redistribution of the impregnated species, and the support can become inhomogeneously covered by the active material in the final catalyst.

In the wet impregnation technique (also called soaking or dipping), an excess of solution is used. After a certain time, the solid is separated from solution, and the excess solvent is removed by drying. The amount of the active precursor mounted onto the porous carrier, its concentration profile within the carrier grains, and its chemical environment on the support surface depend significantly on the conditions during these first two steps in catalyst preparation.[159] Under equilibrium conditions, the amount introduced onto the porous support depends on the equilibrium concentration of the impregnating solution, the porous volume of the carrier, and the adsorption isotherm which describes the binding of the precursor onto the support surface.

The concentration profile of the impregnated compound depends on the mass transfer conditions within the pores during impregnation and drying. When strong precursor–support interactions occur through chemical or physical forces (surface hydrolysis, ligand substitution, ion exchange, electrostatic attraction), the amount immobilized on the pore walls of the support can exceed that of the dissolved substance which remains in the pore filling solution; the resulting catalyst is designated as sorption type.[159] Under nonequilibrium conditions of impregnation, the distribution of the impregnated component is dictated by a sorption–diffusion mechanism and is only slightly affected during drying. The opposite case is that of impregnation-type catalysts.[159] Here, the dissolved component dominates because of the lack of significant solute–support interaction or because of too large a concentration in the pore solution; the concentration profile is determined by mass transport during precipitation–crystallization of the dissolved component which, in turn, is controlled by the conditions during solvent evaporation.

The control of the impregnation profile for preshaped supports is important for preparation of commercial catalysts. In general, the sequence of fast processes at the oxide/solution interface and slow diffusion within the porous structure of the solid results in a diffusionally controlled sorption regime. Under the condition of strong precursor–support interaction, the concentration profiles of the impregnated materials are, in general, nonuniform; they can, however, be manipulated when equilibrium conditions are realized by either modifying the interfacial chemistry between the impregnant and the support[208,209] or by using impregnation coingredients. According to the classification scheme proposed by Schwarz and Heise,[210,211] solution ingredients have effects on the ionic strength (modifying the thickness of the electrical double layer at the interface), on solution pH (altering the surface potential and eventually partially dissolving the oxide surface), or on the adsorption sites (competing with the precursor species for the same adsorption sites).

Coimpregnation techniques were recently applied to molybdena/alumina catalysts[212] and to deposition of noble metals on monolith supports.[213] The impregnation kinetics and the temporal evolution of concentration profiles can be predicted on the basis of Fickian diffusion and by considering various types of adsorption isotherms. Ruckenstein and Karpe[214] accounted for the effects of ionic strength, surface dissociation and electrokinetic phenomena on distribution profiles of impregnant and coimpregnant. Chou et al.[215] combined the triple-layer theory with transport equations and modeled the Ni/Al_2O_3 system which is, however, atypical of the classical pattern resulting from electrostatic adsorption. In general, introduction of adjustable model parameters cannot be avoided, and the value of several models to predict the results of various impregnation modes was recently compared.[164] Still, a practical design equation for metal distributions under nonequilibrium conditions of preparation for the Ni/Al_2O_3 system was successfully advanced by Zhang and Schwarz.[216]

2. Homogeneous Deposition–Precipitation

The method of deposition–precipitation was developed to overcome the problems cited above. When accompanied by adsorption, this method can provide a well-dispersed and homogeneous active precursor even though the metal content is high.[217,218] This method found its greatest utility when applied either to deposition of nickel[217–220] or copper[221–224] on either alumina or silica.

The chemical processes occurring involve a reactant which transforms the catalyst precursor into an insoluble form which is generated slowly in solution, and its concentration is raised homogeneously. When nucleation first occurs, the precipitate is deposited exclusively (adsorbed) onto the support. Practical realization demands that the nucleation rate is higher at the surface than in the bulk of solution and that the homogeneity of the bulk solution is preserved. This is possible by separating the steps of addition and reaction of the precipitating agent, for example, using the hydrolysis of urea at 360 K as a source of OH^- ions. Besides the hydrolysis of urea, other reactions were proposed as shown schematically in Figure 6. Recently, the technique was used to prepare in a single step $MoS_2/\gamma\text{-}Al_2O_3$ catalysts by thioacetamide hydrolysis, bypassing the conventional steps to prepare supported molybdenum oxide.[225]

A second procedure uses injection of the precipitating agent below the surface of the suspension containing the solid support and the precursor compound. Under the conditions of vigorous agitation, a rapid distribution of the precipitant can be realized and precipitation occurs homogeneously. The scale-up of the procedure is however not straightforward because of the requirement for a high shear stress of the support suspension.

In the electrochemically controlled procedure, the precipitating agent is generated at either the anode or the cathode of an electrochemical cell.[218] The method offers the advantage of fine control of the pH and the valence of the ions to be precipitated; also, anodic dissolution of a metal can be combined with its deposition–precipitation onto a suspended support.

The variants of redox deposition–precipitation exploits the fact that reduced or oxidized forms of several metals are insoluble. A change of oxidation state is induced in a homogeneous solution, making use of a redox agent; the insoluble form is deposited preferentially over the suspended catalyst support. An example is the reductive deposition of metallic silver from a homogeneous solution of silver amine; highly dispersed silver nuclei anchored on alumina were obtained.[226]

It would appear that, of the techniques discussed above, incipient wetness impregnation and deposition–precipitation are specific for systems with weak interaction or without any interaction at all between

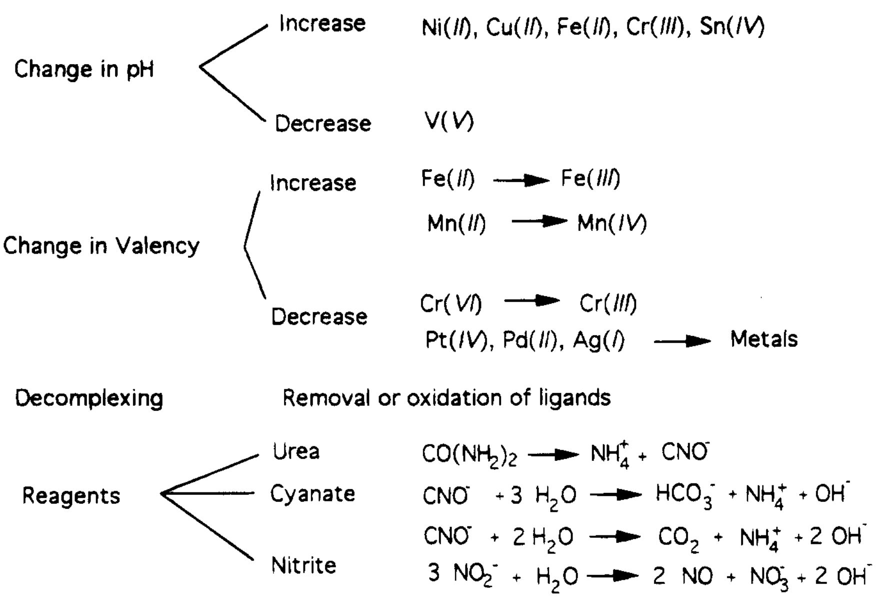


Figure 6. Reaction sequences developed for deposition–precipitation onto suspended solids.

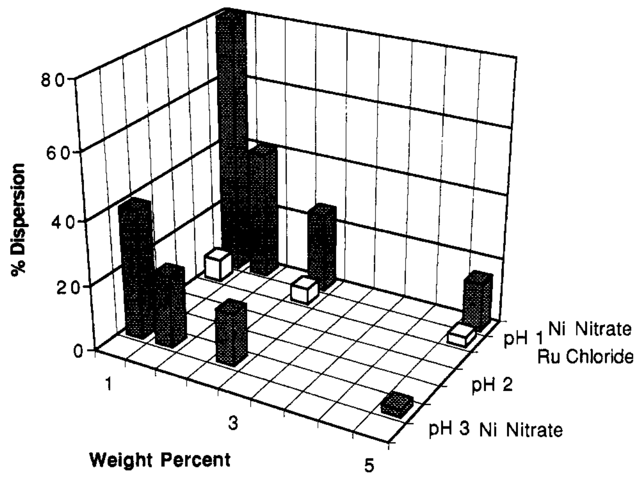


Figure 7. Effects of electrolyte pH and weight loading of nickel and ruthenium on their dispersions.

precursor and support. The development of characterization techniques of catalysts during various stages of preparation has shown, however, that this is not always the case. For example, mounting high concentrations of Ni on alumina by the incipient wetness technique requires a high concentration of metal salts. For reagents, such as $Ni(NO_3)_2$, an increase in solution concentration results in lower solution pH which influences the dissolution of the support.[227] Such effects were found when preparation variables (Ni content, impregnant pH) were examined in relation to the catalytic performance of Ni/Al_2O_3 prepared by incipient wetness.[228] Changes in metal concentration dramatically affected the dispersion of Ni. In this system, the metal dispersion and the partitioning between surface Ni and Ni incorporated in the support depended also on the crystallinity of the support, a factor which determines its dissolution properties.[229] On the other hand, the dispersion of Ru/Al_2O_3 prepared by incipient wetness was relatively unaffected by increases in weight loading because the ruthenium salt affords a better buffering of the (acidic) impregnation solution.[230] It was proposed that dissolution of alumina facilitates continuous generation of anchoring sites and thus higher amounts of salt precursor can be effectively dispersed by incipient wetness[231] as depicted in Figure 7.

Exploiting the deposition–precipitation technique to achieve high dispersion and homogeneous deposition even at high metal loadings is also related to the occurrence of strong precursor–support interactions. The technique was successfully used in systems where support interaction compounds may be formed, such as either layered nickel[219,220] and copper silicates,[222] or cobalt aluminate.[232,233] A type of chemical affinity between the precursor and the support must exist which allows for homogeneous deposition by surface precipitation. This affinity can be beneficial to the properties of homogeneously precipitated catalysts resulting in increased dispersion, improved stability against sintering,[222,234] and higher activities.[223,225]

In the cases discussed, the subsequent steps also play important roles during catalyst preparation because they can be accompanied by profound and irreversible transformations of the catalyst. When there is weak or no interaction between the precursor and the support and the washing step after impregnation is not used, the result is that the counterions introduced with the main component remain in the catalyst and can take part in unwanted physicochemical processes. During drying, catalyst redistribution may occur within the pore network of the support. Calcination is usually required in order to transform the metal salt into oxide, and this is sometimes accompanied by chemical bonding at the oxide/support interface. For example, in Co/Al_2O_3 prepared by incipient wetness, a mixture of surface spinel, amorphous cobalt oxide overlayer, and bulk Co_3O_4 was identified;[235] the proportion depends on loading and calcination temperature.[232,233] If catalyst activation is performed by reduction, the size of metal particles depends on the size of the pores and on the extent of the interaction between the oxide and support.[236]

3. Ion Exchange

The method of ion exchange allows for the introduction, in a controlled way, of a precursor from aqueous solution onto the support. The term ion exchange has been used to describe all processes where ionic species from aqueous solution are attracted electrostatically by charged sites on the support surface. The difference between true ion exchange processes and electrostatic adsorption at the charged surface of oxides was not always explicitly considered. For example, in the old literature,[237] introduction of $[M(NH_3)_n]^{z+}$ complexes from basic solutions and of $[MCl_n]^{z-n}$ complexes from acidic media on alumina were regarded as ion exchange processes. Now there is sufficient evidence which proves that more complex chemical transformations, rather than simple ion exchange, occurs when Pd or Pt complex species with Cl^- or NH_3 ligands are introduced onto alumina[238-240] and even silica.[240,241]

Catalyst systems, which require charge compensating ions and have received the most attention as versatile materials suitable for ion exchange, include zeolites, cationic clays, and layered double hydroxides. These are ideal ion exchangers because the crystalline lattice bears electric charges. Compensation of electric charges is a prerequisite for stability of the crystalline structure. As a consequence, the lattice charge is compensated by oppositely charged ions bound electrostatically in extralattice positions. These ions are readily exchanged by ions bearing an equivalent charge from aqueous solutions.

Zeolites are cationic exchangers. They combine the unique features of high ion exchange capacity, crystalline structure, and uniform pore sizes. The catalytic properties of noble and transition metals and steric constraints imposed by the zeolite structure have provided a strong incentive for developing reliable procedures to prepare highly selective supported-metal catalysts with narrow particle size distributions. A series of recent works from Sachtler's group studied the steps related to the genesis of zeolite encaged metal particles by the ion exchange strategy with their goal to prepare "catalysts by design".[242]

Preparation of zeolite supported metals by ion exchange[243] involves the exchange of complex amine cations of Pt or Pd with K^+, Na^+, or NH_4^+ ions:

$$Pt(NH_3)_4{}^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)} + K^+{}_{zeol} \Leftrightarrow 2K^+{}_{(aq)} + 2Cl^-{}_{(aq)} + Pt(NH_3)_4{}^{2+}{}_{zeol} \quad (14)$$

The co- and counterions, in this example K^+ and Cl^-, are removed by filtration and washing. On the other hand, if incipient wetness impregnation is employed, these ions remain in the zeolite. The ion exchange step places the amine-coordinated ions in the supercages. The next step is the destruction of the NH_3 ligands by calcination which produces PtO particles and Pt^{2+} ions coordinated to zeolite walls; in contrast, an unknown distribution of Pt^{4+} and Pt^{2+} is obtained by incipient wetness.[244] Complications arise from side phenomena which accompany the calcination and reduction step:[242,245,246] migration of metal ions into smaller zeolite cages where their reduction requires higher temperature; autoreduction of metal ions by decomposing NH_3, which causes agglomeration of larger particles; proton generation during metal reduction which changes the acidity of the catalyst. These undesired processes can still be controlled. For example, reduction of zeolite-encaged Co^{2+}, Ni^{2+}, and Fe^{2+} is much easier if a noble metal (Pd, Pt) is present in close proximity;[247] $PdNi_x$ alloy particles encaged in NaY zeolite were obtained after simultaneous ion exchange with $Pd(NH_3)_4{}^{2+}$ and Ni^{2+}.[248] Blocking small size channels with less reducible, high charge density ions (Ca^{2+}, Sr^{2+}, Mn^{2+}) forces Co^{2+} and Ni^{2+} to remain in supercages.[249] Small metallic clusters of Pt and Pd can be anchored to zeolite walls by transition metal ions (Fe^{2+}, Cr^{3+}, La^{3+}, Ce^{3+}).[250] This type of "chemical anchoring" increases the dispersion and thermostability of the noble metal particles. Exposure to water vapor after calcination, but before reduction, is detrimental to metal dispersion because of the increased mobility of $Pd(H_2O)_n{}^{2+}$ complexes formed.[251]

Layered silicates which comprise the natural clay mineral group (smectites, vermiculites, chlorites) are lamellar compounds with negatively charged layers. The layer charge is compensated by interlayer cations. In polar solvents, the layers swell, and the interlayer cations become accessible and exchangeable.

A simple ion exchange reaction from aqueous solution may be used for intercalation of hydrated metal ions, $[M(H_2O)_m]^{z+}$, and cationic metal complexes, $[ML_m]^{n+}$. Immobilized metal complexes have quite similar catalytic properties as their counterparts in homogeneous solution, although selectivity modifications may be induced in the intercalated catalyst by steric factors and the increased acidity in the interlayer space.[252] Calcination leads to immobilized metal ion catalysts. Many important catalysts for organic reactions, especially those involving protonic processes, were derived from cation-exchanged montmorillonites, hectorites, beidellites, and smectites.[253] The subject was recently reviewed by Morikawa.[254]

In addition to producing changes in the chemical composition and resulting catalytic activity, ion exchange can also be used for these materials as a method to modify the size and accessibility of the internal pores, i.e., the secondary structure. For example, the pore structure and the morphology of the monovalent 12-heteropoly oxo metalate salts possessing the Keggin structure can be altered by ion exchange; a microporous structure was obtained for a series of $K^+/NH_4^+/PM_{12}O_{40}$ (M = W or Mo) salts.[255] Also, the two-dimensional character of lamellar compounds can be gradually weakened or enforced by intercalation through ion exchange.[256] In this respect, ion exchange is an excellent and versatile method for preparation of new classes of molecularly engineered layered structures. Pillared materials are the most significant.

Pillared analogs of layered materials have been extensively studied as catalysts.[254,257] They are prepared by intercalation through ion exchange of oligomeric metal hydroxide cations, $[M_x(OH)_y]^{n+}$, within the negatively charged layers of natural or synthetic clays. The nature of the host clay and that of the intercalated polycation gives rise to different catalytic properties. The most popular pillaring agent is the Keggin-like ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$; however, studies were conducted with other metal oxide aggregates derived from Ni, Zr, Si, Fe, Cr, and Ti. The versatility of these materials is related to the microporous structure that can be modified using pillars of various structures and chemical compositions.[258] For example, a new iron oxide pillared montmorillonite with a large gallery height (28 Å) was prepared and tested as a Fischer-Tropsch catalyst.[259] The interested reader is referred to several recent reviews[254,260,261] which summarize the potential of these materials as catalysts.

Layered double hydroxides which are the anionic analogs of cationic clays are rarely found in nature. Their structure consists of cationic layers which bear positive charges and are intercalated with electrostatically held anions of the general structure $M_a^{2+}M_b^{3+}(OH)_{2a+2b}(X^-)_b{\cdot}xH_2O$ where M_a may be Mg, Fe(II), Co, Ni, Zn and M_b may be Al, Cr, Fe(III). The most common structures are derived from hydrotalcite and mannaseite. The anion exchange of these materials is not as easily achieved as for cations in clays. The reason is a much higher charge density and a tenacious bonding of CO_3^{2-} when this is X^-. Methods to solve this in order to prepare pillared derivatives were discussed by Jones.[262]

4. Colloidal Events: Electrostatic Adsorption

Most oxide supports develop pH-dependent surface charge when immersed in aqueous solution, according to the general equilibria

$$\equiv S{-}OH_2^+ \leftrightarrow \equiv S_{basic}{-}OH + H^+ \qquad (15)$$

$$\equiv S_{acid}{-}OH + OH^- \leftrightarrow \equiv S{-}O^- + H_2O \qquad (16)$$

where $\equiv S_{basic}{-}OH$ and $\equiv S_{acid}{-}OH$ represent hydrated sites at the oxide surface with basic and acidic character and may have different local configurations. Depending on the concentration of either one or another type of site, oxides may show a dominant tendency for adsorption of cations (SiO_2, $SiO_2{-}Al_2O_3$, zeolites), of anions (MgO, La_2O_3, ZnO), and both, namely cations in basic solutions and anions in acidic solution (Al_2O_3, TiO_2, Cr_2O_3). For nonmicroporous oxides, the surface charge development depends on solution variables (pH, ionic strength); this is in contrast to the case of most microporous solids with true ion exchange character due to the charge of the crystalline framework. For impurity-free catalyst supports, there are no ions on their surface, other than H^+ and OH^-, that can react with charged species from the impregnation solution.

In modeling catalyst preparation by electrostatic adsorption, at least three elements are needed: the pH-dependent surface development of the support, the pH-dependent speciation of the precursor in the impregnation solution, and a model to describe the surface interaction.[263] The adsorption properties of various oxides as a function of solution pH may be predicted, at least in principle, by a knowledge of their apparent point of zero charge (PZC).[264] However, the heterogeneity of acid/base sites on their surface raise some questions as to the significance of a global PZC. To predict the pH-dependence of surface charge, knowledge of the distribution of proton binding properties for various surface sites (strength and number) is needed.[196]

The chemical speciation of catalytic precursors depends on the properties and concentration of the precursor salt, the solution pH, ionic strength, and the presence of added or extraneous counterions. This "bulk-type" chemistry of solute species is probably the best defined of the three elements above.[265,266] As an example, the effect of solution speciation on adsorption in the Pd/Al_2O_3 system[239,267,268] and of solution precursors on the dispersion of Ru/Al_2O_3 catalysts[230] were investigated.

For small ions, it is generally accepted that adsorption is predominantly electrostatic in nature, although many examples can be cited when electrostatic interaction is the first step before stronger chemical bonds are formed. The prevalence of an electrostatic mechanism in many solute–support systems is supported by those experimental results where the extent of adsorption of positive (negative) ions increased when pH increased (decreased). This general trend is related with the charge development according to surface ionization reactions (eqs 15 and 16) and correlates with the apparent value of the PZC of oxidic supports.

There have been several studies related to adsorption of ions of catalytic interest on different oxide supports. Brunelle[264] has proposed an adsorption model which places emphasis on electrostatic aspects. Although individual adsorption processes may be unique, general rules were derived for adsorption of anions[269,270] and cations.[271] The conclusion of practical interest to catalyst preparation is that the solution variables that can be controlled by the experimentalist during preparation are the initial concentration of the precursor, pH, and ionic strength of the impregnation solution. The final concentration of catalytic precursors is strongly dependent on these three variables, either directly or through indirect effects (support dissolution, solution buffering, etc.).[272]

Equilibrium adsorption results in high metal dispersion, but the loading achieved may be insufficient in some precursor/support systems for preparation of interesting catalysts. This is because, usually, the surface density of adsorption sites is low. Studies devoted to elucidating the adsorption mechanism for ions on the surface of γ-Al_2O_3, SiO_2, and TiO_2 have shown that adsorption sites for negative ions (e.g., MoO_4^{2-}, WO_4^{2-}, $PdCl_4^{2-}$) are neutral or protonated hydroxyls.[268,270,273–277] For the same oxides, sites for adsorption of positive ions (e.g., Co^{2+}, Ni^{2+}, Cr^{3+}, $Ni(NH_3)_6^{2+}$, $Co(NH_3)_6^{2+}$, $Pd(NH_3)_4^{2+}$) are deprotonated surface hydroxyls.[174,196,268,278–281] From a detailed analysis of adsorption isotherms, Lycourghiotis et al.[274–276,278] concluded that under equilibrium adsorption conditions, the adsorbate ions (either positive or negative) were located at the inner Helmholtz plane (IHP) of the double layer developed between the support surface and the electrolyte. Adsorption led to the displacement of water molecules. It has been also shown that lateral interactions are usually exerted between the adsorbed species through the water molecules located at the IHP.

Doping of solid oxides with electropositive (Na^+, Li^+) or electronegative (F^-, Cl^-) ions results in the increase/decrease of the apparent PZC values of supports.[282-284] Lycourghiotis et al. attempted to regulate the adsorption capacity of amphoteric supports for cations or anions by this method.[285,286] However, the introduction of basic or acidic modifiers may also change important properties of the catalyst. To overcome this disadvantage, a second procedure was proposed, namely to vary the temperature of the impregnation solution, which would modify the equilibrium constants for protonation/deprotonation of surface sites and therefore the number of charged sites on oxides.[287]

When adsorption controlled by electrostatic effects is conducted on a composite oxide support, new possibilities for molecularly engineered preparations are created. Composite oxides in which the second component is well dispersed but with a part of the surface of the host oxide still remaining exposed, offer unique properties for the introduction of catalytic metals. Controlled pH regulation of the impregnating solution may result in a selective adsorption of precursor ions either on one, on the other, or on both of the oxide components. The concept of selectively adsorbing metal ions on one of the components of a composite oxide can be applied to cations (e.g., $Pd(NH_3)_4^{2+}$ and Cr^{3+} were adsorbed selectively on silica in Al_2O_3/SiO_2 supports[279,288]) as well as anions (e.g., $PtCl_6^{2-}$ and $IrCl_6^{2-}$ were selectively partitioned to alumina in TiO_2/Al_2O_3 supports[289]). The same concept was applied to mount a secondary metal activator (Ni^{2+}, Co^{2+}) by aqueous impregnation in WO_3/Al_2O_3 composite oxides. The development of surface charge and the chemistry of dispersed tungsten species in an aqueous environment can be best described by analogy with that of an alumina support at low tungsten loading; it replicates the aqueous speciation of polytungstates at high WO_3 loading.[204] Equilibrium adsorption of cobalt[290] or nickel[291] on these composite supports leads to the formation of stable association compounds between the cations introduced and the negatively charged tungsten species whose properties correlate with the most stable forms of aqueous tungsten species at the pH of the impregnation solution.

Other experimental evidence exists that is not easily interpreted within the framework of the electrostatic model for adsorption on oxide surfaces with only one type of amphoteric surface site. Exceptions from the simple rule of electrostatic adsorption were regarded as examples of "specific" or "chemical" surface–adsorbate interactions which may compete with coulombic repulsion.[292,293] This phenomenon, however, is not an exception, as evident from examples which include adsorption of cations (Ni^{2+}, Co^{2+}, Pb^{2+}) onto a positively charged alumina surface[215,278,292,294] and of molybdate[284,295] or tungstate[296] anions on negatively charged alumina.

When the effect of pH was systematically investigated, it was found that the loading curves show apparent discontinuities which could not be explained by a simple electrostatic mechanism. Wang and Hall[270] suggested the existence of different crystal planes of alumina, with different local isoelectric points, is responsible for the observed breaks of the loading curves for molybdate and tungstate ions as a function of pH. Maxima and minima also occurred for adsorption of Cu, Ni, and Co from ammonical solutions onto various oxides, and they paralleled charge reversal observed in electrophoresis experiments.[297]

The cited examples suggest the existence of particular sites on the hydroxylated surface of commonly used supports that act specifically in adsorption of the catalyst precursors; they also demonstrate that these sites are related to the intrinsic acid/base properties of the surface. When different types of sites are involved, they act as sites for distinctly bound adsorbed ions.[284]

Although a definitive adsorption model has not yet been established, the picture that emerges from the recent literature in this field emphasizes the importance of the intrinsic heterogeneity of adsorption sites (surface hydroxyls) on oxidic supports. The concept of heterogeneity coupled with a charging mechanism that predicts the occurrence of variable amounts of positive and negative sites as a function of pH[195] offers a more consistent explanation of these experimental results. The description of charge development at aqueous alumina surfaces proposed by Contescu and Schwarz[196] accounted for geometrical constraints between the size and shape of the adsorbing ions and the ensembles of charged sites existing at the surface which may also be important factors that determine the amounts adsorbed. This is an additional factor to be added to the classical model introduced by Brunelle[264] for preparation of catalysts in which electrostatic attraction of adsorbing ions by an essentially uniform oxide surface was assumed.

5. Coordinative Events: Grafting by Hydroxyl Interactions

It was perhaps not by coincidence that two pioneering papers on catalyst preparation were published in the same year, 1978. One is the paper in which Brunelle[264] demonstrated the importance and versatility of electrostatic adsorption in catalyst preparation; the other is the publication in which Summers and Ausen[238] demonstrated the occurrence of an alternate mechanism for precursor bonding during catalyst impregnation, namely adsorption by ligand substitution. The latter authors studied the reaction of amine complexes of Pt, Pd, Rh, Ir, Au, and Ru with alumina and suggested that there are two reaction pathways during equilibrium adsorption. One of these involves displacement of ligands from the coordination sphere of the adsorbate complex; this was the case with complexes containing halogenides as ligands. The other pathway which does not involve ligand substitution was observed for complexes of the type $[M(NH_3)_4]^{2+}$ and $[M(NH_3)_5Cl]^{2+}$, which are adsorbed electrostatically. Since then, other examples of adsorption of complex ions through partial substitution of their ligands by surface hydroxyls have been reported.

Olivier et al.[298,299] studied adsorption of amine complexes of Cu^{2+} and Ni^{2+} on silica. In aqueous ammonium hydroxide these ions are stable as $[M(NH_3)_n(H_2O)_{6-n}]^{2+}$ ($n \leq 5$), and the species that resulted on adsorption on silica were defined as $M(NH_3)_4(SiO)_2$, with substitution of two water ligands by $Si-O^-$ groups. According to others,[300] adsorption of amine complexes of Co^{2+}, Ni^{2+}, and Cu^{2+} on titania proceeds by direct coordination through surface oxygen after displacement of one NH_3 ligand.

In the case of adsorption of oxyanions on various supports, the establishment of a definitive model still seems to be lacking. Meunier et al.[301] reported that a similar number of oxyanions were adsorbed at constant pH on alumina, regardless of the nature of the metal. However, Mulcahy et al.[277] concluded that there existed some metal specificity: MnO_4^- and ReO_4^- were weakly adsorbed on alumina by electrostatic forces only, while $Mo_7O_{24}^{6-}$ and $W_{12}O_{39}^{6-}$ ions produced loosely and tightly bound surface species in the acidic pH range, according to the following mechanisms:

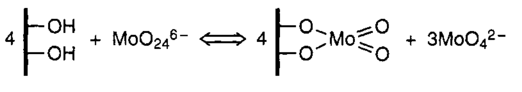
electrostatic adsorption

$$\equiv Al-OH_2^+ + Mo_7O_{24}^{6-} \Leftrightarrow \equiv Al-OH_2^+\cdots Mo_7O_{24}^{6-} \quad \text{(loosely bound)} \quad (17)$$

grafting by condensation with surface hydroxyls

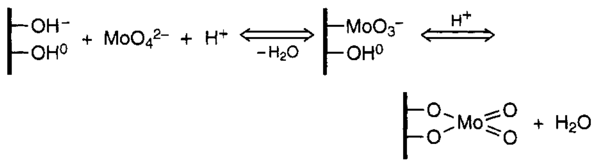
$$\equiv Al-OH_2^+\cdots Mo_7O_{24}^{6-} \Leftrightarrow \equiv Al-O-Mo_7O_{23}^{5-} + H_2O \quad \text{(tightly bound)} \quad (18)$$

A different mechanism, but still involving direct reaction with the basic surface hydroxyls at pH 5–6, was proposed by van Veen et al.:[302]



(19)

The interaction of molybdate species with the basic hydroxyls on alumina surfaces was demonstrated by a substantial decrease in IR intensity of surface −OH species; a typical surface reaction in the basic pH range was proposed by Okamoto and Imanaka:[303]



(20)

The MoO_3/Al_2O_3 catalyst is only one example of technological importance within the broader framework of a series of systems of catalytic interest. When one metal oxide component (Re_2O_7, CrO_3, MoO_3, WO_3, and V_2O_5) is deposited on a second high surface area oxide substrate (Al_2O_3, SiO_2, and TiO_2), two-dimensional oxide overlayers are formed. These systems represent a class of catalysts which has witnessed an increased interest in recent years. The reader is referred to the review by Wachs and Segawa[304] who updated information existing on the preparation and properties of supported oxides. They are typically prepared by impregnation from aqueous media. The properties of these materials are critically conditioned by the nature of the interfacial interaction between the parent precursor species and the support. These interactions may be purely electrostatic in nature, but in most cases, a stronger and specific interaction, which results in the dispersion and stabilization of the oxide coating, was demonstrated. In favorable cases, the precursor species introduced from the liquid phase interacts through ligand exchange, in which the support hydroxyls enter the coordination sphere of the adsorbate. A subsequent thermal treatment results in stabilization of a molecularly dispersed oxide. Nonspecific bonding is detrimental because weakly bound species may migrate and aggregate into bigger particles. The factor which decisively influences the tendency toward monolayer formation in the various systems investigated so far appears to be the particular reactivity determined by differences in the acid/base character of the dispersed and host oxide and, to a lesser extent, the method of preparation.[305] Thus, polymeric species of chromium oxide were detected on Al_2O_3, TiO_2, ZrO_2, and Nb_2O_5, but isolated chromate species were stable on SiO_2 (the most acidic support) while products of much stronger interaction, such as $Mg_x(CrO_4)_y$ were found on MgO (the most basic support).[306-308] A continuous consumption of the OH^- groups, starting with the most basic hydroxyls, was observed upon deposition of a series of oxides (Re_2O_7, CrO_3, MoO_3, V_2O_5, TiO_2, Nb_2O_5) on alumina.[186] Wachs showed that the molecular structure under ambient conditions of two-dimensional metal oxide species dispersed on oxide supports depends on the pH at the PZC of the composite; oxide supports possessing predominantly basic properties were found to favor molecular aggregates that are stable in basic solutions and vice-versa.[185] This fact suggests that the preparation method does not affect the molecular structure of the surface metal oxide species;[309] only the presence of surface impurities/dopants, variations in surface concentration and changes in dehydration temperature can influence the final PZC and thus the predominant charge structure of the dispersed oxide species.

6. Molecular Events: Formation of Chemical Compounds

Very often it is difficult to delineate between the interactions which modify the inner coordination sphere of the deposited precursor and those resulting in new chemical compounds formed on the surface of the impregnated catalyst. There is a gradual transition between these possibilities, and slight changes during preparation may result in completely different impregnated products, even for the same system at comparable concentration levels of the adsorbate.

We take the example of nickel/silica catalysts which formed the basis for study by several groups of investigators. The nickel nitrate precursor deposited by impregnation is weakly held and easily washed off, but drying for a long time at 360 K lead to the intermediate formation of basic nitrates and finally of 1:1 nickel phyllosilicates (containing about 20% nickel).[310] If preparation is conducted with nickel amine, the ion $[Ni(NH_3)_6]^{2+}$ is held electrostatically at pH > 9.5, but at lower pH $[Ni(H_2O)_x(NH_3)_6]^{2+}$ ions, which predominate in solution, interact strongly with the carrier giving rise to the formation of layered nickel silicates.[174] If the nickel complex is protected against hydrolysis by replacing NH_3 ligands with ehylenediamine, only electrostatic adsorption occurs and silicate formation is not observed.[311] The role of drying is evident: the removal of amine ligands from the coordination sphere of electrostatically adsorbed complexes leads to formation of silicates. Calcination of these samples gives rise to surface nickel nuclei which strongly interact with the support; their chemical nature depends on the preparation method. For example, basic nickel nitrate, $HO-Ni_{imp}$ results by drying catalysts prepared by incipient wetness; nickel incorporated in the phyllosilicate, $Si-O-Ni_{nucl}-OH$, is formed at longer drying times or higher temperatures; grafted nickel, $Si-O-Ni_{nucl}-OH_2$, results from electrostatically bound ethylenediamine complexes.[187,312] On the basis of this observation, Che proposed a two-step procedure for preparation of Ni/SiO_2 catalysts with controlled particle size distribution. In the first step, nickel nuclei are formed on the surface. Deposition of nickel nitrate by incipient wetness impregnation during a second step leads to a "nickel reservoir" in weak interaction with the support and easily reducible. During drying at 360 K, nickel nitrate transforms to basic nickel nitrate, $HO-Ni_{imp}$, whose OH groups can react with those of the nickel nuclei which acts as anchoring sites for the growing NiO particles:

$$Si-O-Ni_{nucl}-OH_2 + HO-Ni_{imp} \rightarrow Si-O-Ni_{nucl}-HO-Ni_{imp} + H_2O \quad (21)$$

or

$$Si-O-Ni_{nucl}-OH + HO-Ni_{imp} \rightarrow Si-O-Ni_{nucl}-O-Ni_{imp} + H_2O \quad (22)$$

The most important consequence is that for a given nickel loading, the particle concentration is determined by the dispersion of nickel anchoring sites; in other words, it is possible to obtain a decrease in metal particle size although the total Ni loading increases.[187,312]

A literature survey shows that small metallic particles supported on conventional oxides often appear to be raft-like, wetting the substrate surface; they may form irregular agglomerates several monolayers thick. Small metal particles are usually not completely reduced; there is a transition region at the oxide–particle interface where accommodation of lattice strain and of oxidation state between reduced metal and underlying support takes place. This is called "chemical glue" [180,181] and is not limited to the Ni/SiO_2 system. In the $Fe-Rh/SiO_2$ system, Fe(III) ions at the interface between support and reduced Rh particles serve as anchoring sites for Rh.[313] A similar interaction was found for Sn(II) and Pt supported on alumina.[314] Electron-defficient palladium was identified in reduced Pd/Al_2O_3 catalysts[315] and is probably located at the metal/support interface.[316] Two chemically different entities of PdO on γ-Al_2O_3 prepared by incipient wetness were identified by XPS; they differ by dispersion and reducibility. The most dispersed particles exhibit an unusually low reducibility.[317] A better knowledge of the metal/support interface is evidently needed for a more efficient regulation of the properties of dispersed small metallic particles.

B. Mounting Dissolved Precursors from Organic Media

Direct grafting of precursors through interaction with the hydroxyl groups on the support surface is a method to disperse the active element in a stable state possessing a strong interaction with the support. Schematically, equilibria such as the following

$$-S-OH + ML_{x-n}(H_2O)_n \leftrightarrow -S-OH-ML_{x-n}(H_2O)_{n-1} + H_2O \quad (23)$$

or

$$-S-OH + ML_{x-n}(H_2O)_n \leftrightarrow -S-OH-ML_{x-n-1}(H_2O)_{n-1} + L \quad (24)$$

describe a process of grafting to surface hydroxyls from aqueous solution. In water, the metal ion is shielded by coordinated ligands, including water molecules, and the probability of substitution reactions like those shown above is not very high. A substantial increase in reactivity may be gained if the aqueous medium is replaced by an organic solvent:

$$-S-OH + ML_x \leftrightarrow -S-OH-ML_{x-1} + L \quad (25)$$

The use of chemical reactions between hydroxyl groups of the support and various active catalyst precursors was an important development in achieving molecular dispersion of metals and oxides supported on oxide carriers. Metal–organic complexes, metal clusters, and other reactive metals species are capable of reacting directly with the surface hydroxyls to form covalent-like chemical bonds. The literature on "molecular" and cluster-like metal catalysts attached to inorganic oxides was reviewed in several recent publications.[170–172,318,319]

Undisputably, metal carbonyls are the compounds used most frequently in the preparation of these catalysts. Next in interest have been metal allyls and metallocenes. Acetylacetonates,[320,321] organometallics, and alkoxides[322] were also used.

SiO_2, Al_2O_3, MgO, and some zeolites have been the most extensively studied supports. Three methods were used to load transition metal carbonyls onto supports: dry mixing, impregnation or adsorption from solutions, and adsorption from the vapor phase. The second gives the best results in terms of homogeneity of the product. Benzene, cyclohexane, and pentene have been used as solvents for mono and polynuclear carbonyls, and various interaction mechanisms were proposed, including electrostatic attraction, ligand exchange, adduct formation with surface basic sites, oxidative addition of polynuclear clusters, and ligand elimination.[318] One of the advantages of this preparation route is that catalysts contain only the active precursor and are free of any accompanying ions.[323] In addition, well-defined molecular structures for the active sites may be designed and prepared.

As an example, we cite Mo/SiO_2 catalysts. When prepared by air- and water-free reaction between $MoCl_5$ and the hydroxyl groups of silica (grafted catalysts[324]), the active phase has different properties compared with impregnated Mo/SiO_2 catalysts. Grafted Mo interacts more strongly with the silica support than impregnated Mo; it is more difficult to reduce and better dispersed on the surface of silica. According to the recent results by Louis and Che,[324,325] oxidized grafted samples contain isolated tetrahedral dioxo Mo species and small MoO_3 clusters, whereas impregnated catalysts consist mainly of larger MoO_3 crystallites and tetrahedral Mo covered by octahedral Mo. The difference in Mo species results in their different behavior in catalytic oxidation of methanol, which is a structure-sensitive reaction. Grafted catalysts show a higher selectivity for methyl formate when compared to impregnated catalysts, whose main product is formaldehyde. We leave it to the interested reader to seek specific details using the most recent reviews of this preparative procedure.[318,319]

C. Mounting Precursors from the Vapor Phase

The method of chemical vapor deposition allows direct deposition of the active material onto catalyst supports, usually under low-pressure conditions. This method circumvents the processes of impregnation, washing, drying, calcination, and activation which are involved in solvent-assisted catalyst preparations. Other complications caused by the solvent (water, in most cases) during liquid-phase preparation, such as dissolution, surface poisoning, and redistribution of the active material during drying, are also eliminated. Another advantage is that the texture of the support is either conserved or can be finely tuned as, for example, control of the pore-opening sizes of zeolites.

The CVD method designates any process of deposition using reaction between surface sites, such as −OH groups on inorganic supports, and vapors of an active material. The compounds that may be deposited from the gas phase are very different. For preparation of dispersed metal catalysts, volatile metal chlorides such as $SnCl_4$ or $NiCl_2$ were used to obtain Pt−Sn/Al_2O_3[326] or Ni/Al_2O_3 catalysts.[327] Loading of metals into molecular sieves was accomplished by vapor phase impregnation, using the volatile Pt(acac)$_2$ complex.[328] Metal loading of molecular sieves in this way has two advantages. First, it is possible to mount metal onto supports with a neutral framework as well as a charged framework, which would not be possible by ion exchange from electrolyte solutions. Second, metal loading by vapor phase impregnation does not alter the acidic properties of the original carrier because protons are not exchanged with a liquid phase during preparation.[328]

Metal oxide films deposited on supports were prepared from volatile alkoxides (vanadyl triisopropoxide[329−331] for deposition of V_2O_5 on SiO_2 and TiO_2; tetraethoxysilane[332,333] for deposition of SiO_2 on Al_2O_3, triethoxyborane for uniform deposition of B_2O_3 on SiO_2[334]) and metal oxychlorides ($VOCl_3$ for deposition of V_2O_5 on TiO_2[335]). Because the alkoxides possess functional groups that can form chemical bonds with either the support (−Si−O−Al−) or between the deposited oxide (−Si−O−Si−), the structure of the growing film is controlled by two-dimensional chemistry and catalysts with well-defined structures may be obtained. For silica on alumina, a silica monolayer was formed from the beginning of the deposition until it covered the alumina surface almost completely.[333] The site specific deposition is probably due to the properties of the support and the reagent deposited; the greater the difference in electronegativity (or acid−base character), the easier the spreading of the second phase oxide on the support. This conclusion was confirmed in the cases of silica and vanadia overlayers formed through CVD on various supports.[333,336] In addition, layer-by-layer growth by chemical vapor deposition was used for the fine-tuning of the pore-size opening of zeolites (mordenite and ZSM-5[337]).

D. Mounting Precursors from the Solid Phase

The spontaneous monolayer dispersion of oxides or salts on high surface area supports is a widespread phenomenon, and its applications to heterogeneous catalysis were reviewed recently.[338] It was first observed that heating mechanical mixtures of MoO_3 and Al_2O_3 at temperatures between 670−770 K produces catalysts with comparable activity to those obtained by impregnation.[339] The spreading of MoO_3 has been inferred from the results of several characterization methods.[340,341] Similar results have been observed in several bicomponent systems and found application in the preparation of an oxychlorination catalyst ($CuCl_2/Al_2O_3$) and catalysts for synthesis of vinyl acetate (Zn acetate/active carbon) and vinyl chloride ($HgCl_2$/active carbon) from acetylene.[338,339] The interested reader may find additional systems where spreading was observed, and the corresponding temperature domains, in a recent review paper.[338]

The spreading process was phenomenologically termed as solid/solid wetting and its microscopic mechanism remains unknown. A general thermodynamic explanation was offered by Leyrer and Knözinger,[342,343] who assumed that the driving force for the formation of dispersed oxide layers is the change in surface and interfacial free energies. In chemical terms, the influence of hydroxyls on the support surface and the role of water molecules in assisting the transport have been proposed,[344] assuming the following chemical mechanism for the MoO_3/Al_2O_3 system:

$$MoO_{3\,(solid)} + H_2O_{\,(gas)} \leftrightarrow MoO_2(OH)_{2\,(surf)} \quad (26)$$

$$2[OH^-]_{(surf)} + MoO_2(OH)_{2\,(surf)} \leftrightarrow [MoO_4^{\,2-}]_{(surf)} + 2H_2O_{(gas)} \quad (27)$$

Although further study is needed to better understand the role of surface hydroxyls in the spreading mechanism and the nature of Mo species, the fact remains that the spontaneous spreading of MoO_3 on

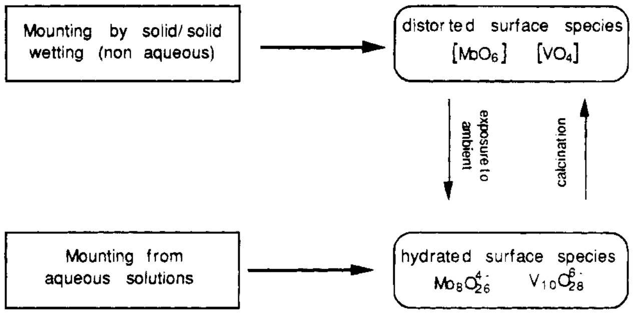


Figure 8. Scheme depicting formation of hydrated surface species by either aqueous or nonaqueous procedures.

an Al_2O_3 support at 770 K in the presence of wet O_2 is an effective alternate method for preparing MoO_3/Al_2O_3 catalysts.[345]

Another system with specific support-active phase interaction is V_2O_5/TiO_2. It is known that the activity of vanadia is enhanced when supported on titania, in comparison with other oxides (silica, alumina). The reason for this is believed to be the occurrence of a crystallographic fit between crystalline planes of vanadia and titania; this is assumed to lead to a natural spreading tendency in the V_2O_5/TiO_2 system[346] and preferential formation of vanadia monolayers via interaction through a V^{4+} interlayer.[347] For industrial use, VO_x layers are mounted on ceramic rings or balls by spraying a suspension of the catalyst onto the support maintained at 720 K.

The molecular design of supported metal oxide catalysts recently became possible.[348] The synthesis method (wet or dry mounting) is not important, since it does not change the chemical reactivity or the structure of surface oxide layers. According to Wachs and co-workers,[309] the preparation method is merely a determinant of the initial state (hydrated or dehydrated) of the catalyst since the same surface species may be obtained from different preparation methods. Thus, the thermal spreading method performed at high temperature is a method of dry mounting which leads only to the dehydrated surface metal oxide species (VO_4, MoO_6). Rehydration of the catalyst surface by exposure to ambient conditions will immediately convert these species to their hydrated analogues ($V_{10}O_{28}^{6-}$, $Mo_8O_{28}^{4-}$) which can be stabilized depending on the PZC condition on the surface.[185] The same species result by mounting precursors from aqueous solutions; their heating in dry air leads to the formation of the dehydrated counterparts (Figure 8). What is apparently important is the specific chemistry at the oxide/oxide interface which is determined by the nature of the metal oxide support and metal oxide overlayer, specifically with respect to the interaction with the surface hydroxyls of the support. Calcination temperature is not important, as long as moderate temperatures (620–720 K) are used.[348]

E. Mounting Preformed Active Phases

To prepare highly dispersed metallic catalysts, the procedure of reducing supported ions has been traditional. Here the active metal is transferred from solution (dissolved salt) onto the support (mounted precursor) and is then either oxidized (calcined catalyst) or reduced without calcination resulting in the active catalyst. The advantage of this route is that it can be easily scaled up at a relatively low cost; the disadvantage is the inefficient use of the metal because of incomplete reduction and uncontrolled sintering during high-temperature salt decomposition and reduction steps.

Controlled thermolysis of organometallic reagents adsorbed on catalyst supports from either vapor or organic liquid phases is a more recent innovation for preparation of catalysts. However, the agglomeration of metal particles after loss of ligands cannot be avoided. Both adsorbed atoms formed by decomposition of mononuclear organometallics and metal clusters resulting from organometallic cluster compounds sinter. Mounting stable organometallics onto supports does avoid high-temperature reduction steps and accompanying sintering; the disadvantage is the limited selection of organometallics that can be used and the difficulty in preparing bimetallic particles.

Mounting metallic atoms or small clusters of metal atoms in their zerovalent state onto appropriate supports appears to be the most straightforward way of preparing dispersed metal catalysts. The atomic state (zerovalent) of the mounted metals eliminates the need for any subsequent activation (reduction), so the catalyst can be obtained, under ideal conditions, in a single preparation step. The problem which must be solved is to find the method for preparation and stabilization of metal atoms and clusters in zero oxidation states prior to their mounting on supports. We have already discussed the preparation of stable colloidal metals and their use as catalysts for reactions in solutions. Colloid metal dispersions are stabilized against aggregation by protecting polymers. Metal atoms require stabilizing agents to ensure their state of dispersion and valency (zerovalent).

The use of organic molecules, which function simultaneously as weak stabilizing ligands and solvents, paved the way for preparation and handling of solutions of solvated metal atoms. One way of looking at such solutions is that the metals have been dissolved in organic solvents in a supersaturated state.[349] They are obtained by evaporating the metal(s) and trapping the atoms in a cold solvent (usually at 77 K).[350] The solutions formed this way are thermally unstable; by warming, nucleation of metal clusters takes place. In the presence of a catalyst support, metal particles grow on the support surface and highly dispersed catalysts can be obtained that were called by Klabunde and his co-workers[349–351] "solvated metal atom dispersed (SMAD) catalysts". Besides the advantage that a high dispersity of the supported metal is conserved, as no reduction step is needed and therefore no sintering occurs, the other advantages of the method are the possibility of obtaining metal particles with special morphology (layered, bimetallic) securely anchored on the support by reaction with surface hydroxyls, and the avoidance of handling toxic organometallics such as carbonyls. On the other hand, the technique is not easily managable, and scaleup has not been demonstrated.[349] However, the catalysts prepared for laboratory applications exhibit a much higher reactivity and

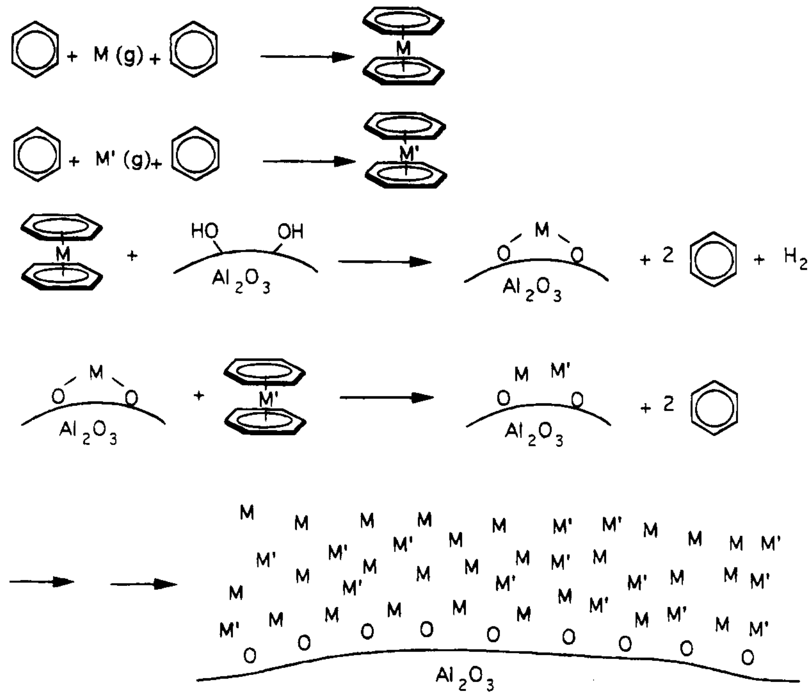


Figure 9. Schematic mechanism for initiation and growth of a bimetallic SMAD catalyst.

selectivity than conventionally prepared catalysts (e.g., by impregnation).[352,353] The method also provides versatility in preparing small bimetallic particles on catalysts (either as layered or as alloy-like structures) which would be difficult to prepare by conventional synthesis schemes.[354,355] Figure 9 illustrates the schematic mechanism for initiation and growth of a bimetallic SMAD heterogeneous catalyst.

Another possibility which was explored[356] was to prepare nanodispersed metal particles without any contact with the support and then to deposit the particles on the support. In the microemulsion technique, metal ions from the precursor salt are dissolved in reversed micelles (oil-in-water type) which are formed, in the presence of a nonionic surfactant, from a mixture of an organic solvent and an aqueous solution of the dissolved precursor. Using a suitable reducing agent, metal ions are reduced "in situ" in the reversed microemulsion without any agglomeration. The stability of the particle suspension is controlled by the concentration of the constituents, the pH, and the temperature. The oxide support is then added to the colloidal metal suspension and the suspension is destabilized to deposit the metal particles to obtain the catalyst. The so-called metal–support interaction was not observed for Pt/TiO_2 catalysts prepared by this method.[357] For Pd/CeO_2 catalysts, surface reduction of cerium was enhanced owing to the presence of palladium metal.[358] Attempts were made to use the microemulsion method for the preparation of Ni–Mo/MgO hydrodesulfurization catalysts[359] and Fe_3O_4/TiO_2 hydrogenation catalysts.[360]

Photoassisted deposition of noble metals is another route that was explored for direct preparation of metal particles dispersed on supports. When a photosensitive semiconductor is illuminated with photons of suitable energy ($h\nu >$ band-gap energy) in the presence of a noble metal salt, metal cations can be reduced at room temperature by the photoelectrons generated while the holes simultaneously produced are consumed by the oxidation of water. As a consequence, the metal can be deposited on small crystallites. Although known for about 25 years, this phenomenon has only been investigated as a method for preparation of catalysts during the last few years.[361-363] The metals used were Pt, Pd, Ag, Rh, Au, Ir; most work was carried out on titania, which shows the highest photoefficiency, but other supports such as ZnO, Nb_2O_5, ZrO_2, ThO_2, and CdS were employed. Recently, quantum-sized TiO_2 particles supported on silica were used as supports for depositing Rh(III) by photoreduction.[364] Different types of bimetallic catalysts with controlled location of metallic phases could also be prepared by photoassisted deposition.[365,366]

V. The Next Dimension

The terms blending and mounting which prevail throughout this review are, admittedly, naive. However, they do capture a sense of the extremes of procedures that are currently within the arsenal of preparative tools available to the catalytic scientist. Within these major categories we find guidelines for producing and reproducing structures at the molecular level that can convert reactants to products and can still survive real-world abuse when used in industrial processes.

There are noticeable "holes" in our presentation. We do not discuss the preparation of either sulfides, nitrides, borides, or carbides, important classes of catalytic materials. The preparation of ionic lamellar solids and bimetallic catalysts has not been covered at any length, and we only touch on multicomponent oxide preparation schemes. Also, there are numerous other materials whose preparational recipes have gone unmentioned. These "holes" exist for the sake

Table 6. New Catalytic Materials and Novel Synthesis Schemes

materials and techniques	examples
physical sequestering or chemical anchoring of metal clusters and/or alloy formation within zeolite cages ("ship-in-the-bottle" synthesis)	Review paper[243] Ir-carbonyls/NaX zeolite[a] $PdNi_x$ alloy/NaY zeolite[b]
preparation of bimetallic catalysts by controlled deposition of the second metal over the surface of the first one ("controlled surface reactions" or "surface redox reactions")	Pd(Ge,Sn,Bi)/Al_2O_3[c] Pt(Bi,Pb,Sn,Ru,Au,Ag)[d] decorated MoS_2/Al_2O_3[e,f] Cu–Ru[g] Cu–Rh/Al_2O_3[h]
sol–gel synthesis of high surface area and thermally stable composite supports for superacidic catalysts with aerogel structure	review paper[i]
catalytic applications of metal-containing fullerenes	transition metal–carbonyl, metal–hydrido and metal–cyclopentadienyl derivatives of C60 fullerenes[j]
use of supported and/or unsupported heteropoly oxometallates as catalytically active phases	various Keggin-type ions[k,l] $H_{3+n}PV_nMo_{12-n}O_{40}$[m]
asymmetric surface modification of supported metal catalysts for synthesis of chiral chemicals	Ni/SiO_2[n] Raney Ni[o]
sonochemistry-assisted preparation of catalysts, amorphous powders, and intercalation compounds	Cr–Mo–O catalysts[p]
zeolites with medium to large pore sizes formed by micelle templation	MCM-22 and variants developed by Mobil[q] Pt/MCM-22[r]

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of establishing some order out of the chaos within the complex scheme of solid state chemistry related to catalyst preparation. One can argue what elements should be contained in a thematic review. We, in fact, have had these arguments between ourselves. As a compromise, we place the responsibility upon the interested reader. Table 6 provides a summary of the most recent literature of new catalytic materials and emerging preparative procedures related to the formulation of those not discussed in detail herein.

Despite the shortcomings of this contribution, there is the recognition of an ever-growing trend to tailor catalysts using the concept of molecular engineering. This must be accompanied by a deeper understanding of why and how certain structures are produced that have the ability to turn over reactants into products. Perhaps in the next thematic review of heterogeneous catalysis we will be in a position to provide such a deterministic delineation.

VI. Acknowledgments

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